THE CORROSION OF IRON

A SUMMARY OF CAUSES AND PREVENTIVE MEASURES

BY

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PREFACE

This little volume is the result of an attempt to collect and put in simple form for reading and ready reference some of the more interesting and important facts connected with the corrosion of iron and its protection therefrom.

It requires no argument to prove the widespread nature and serious import of this process of decay, and the volume of literature to be found on this subject is evidence of the increasing attention which is being paid to it. It is only comparatively recently, however, that corrosion has been studied in a scientific manner and something of its true character ascertained, so it naturally follows that the same thing is true in large degree of the measures employed for protection. This is, perhaps, especially the case with paint pigments and vehicles, where careful experiments have brought to light many fundamental truths of the greatest value regarding the nature and action of some of these materials, thus enabling us to use them with much greater intelligence and effectiveness. Much of the published work, however, is scattered throughout many different scientific and technical magazines, consequently is largely inaccessible to one who does not have the time or facilities for such investigation.

It is accordingly hoped that this book, by presenting some of this material in condensed form, may help to give the student or busy engineer a better understanding of the problems involved in the successful preservation of one of our most useful building materials, and point the way to their solution.

Brooklyn, New York.
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THE CORROSION OF IRON

Chapter I

THE RUST PROBLEM

AMONG the many questions which the architect and builder are called upon to consider, none perhaps, is more important than that relating to the corrosion of iron and steel. This tendency to decay is peculiar to these materials, since none of the ordinary metals exhibits it to any comparable degree, and it is so strong that an unprotected piece is soon reduced to a shapeless mass of rust. It is one thing to design and erect a mighty sky-scraper, but an entirely different matter to protect it from those influences which, if allowed to do their work, would ruin the greatest structure in a short time.

It seems strange, in a way, that unless iron is well protected it is far less resistant to natural agencies than wood or other building materials. It is being used more and more in the fabrication of large buildings and other

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structures of a permanent type, and the length of their life, to say nothing of the safety of the people employed in and around them, depends on the success with which corrosion can be prevented.

Painters are constantly employed on such structures as the Brooklyn or Forth bridges, scraping away rust spots and repainting. When serious rusting is once started it is very hard to check, and as it would inevitably lead to the destruction of the framework, a collapse would be certain to occur sooner or later, probably with an appalling loss of life.

The economic side of the question is also of serious import. It is being recognized more and more that the increasing use of materials is depleting our stock of natural resources, and it is evident that when these are irrevocably lost through some form of decay, we have sustained a real and serious loss. The production of pig iron in the United States alone has increased amazingly until now many millions of tons are produced annually. How much of this is wasted for lack of suitable protection, or otherwise, cannot be stated very accurately, but the total is considerable. How long our ore supply will hold out against the steadily increasing de-

mand can only be vaguely guessed, but if present conditions keep up there is certain to come a time when the scarcity and high price of iron will not permit it to be used so prodigally as now. Again, the coal supply is by no means unlimited, and since it requires about four tons of coal, or its equivalent, to produce one ton of steel, it is apparent that when we allow iron to rust or otherwise go to waste we are losing not only iron, but coal, one of our most valuable assets.

I do not mean to imply that the corrosion of iron is a new problem, or that technologists generally do not realize its importance, since the articles and discussions which have been appearing in the technical press for the last few years are evidence of the work that is being done along these lines. This literature, however, is distributed through a large number of publications and is, therefore, not readily accessible to the busy engineer, so in this small volume an attempt will be made to collect some of this information regarding the study of corrosion and its practical application in the protection of iron and steel, and to present it, together with the results of personal observations and tests, in a simple, compact form.

Before taking up any of the theories as to the nature and cause of corrosion, it may be interesting to note a few points about the process in general. It is a matter of common knowledge that iron soon becomes covered with a heavy coating of rust, if it is exposed to moisture without first being protected by paint or other good preservative, and that in time the piece will be entirely honeycombed and will assume a lace-like appearance. It is also known that different pieces of iron and steel exhibit widely varying tendencies in this respect; that is, some are surprisingly resistant and keep in fairly good shape for a long time even under very adverse conditions, while others soon show the most serious rusting when exposed to the same conditions. The manufacturers of wrought and charcoal irons and the various kinds of steel have each contended strenuously that his particular product is most resistant to corrosion, but it is not the province of this chapter to state who is in the right, since it appears that each of these types of metal may vary greatly in rust resistance and that there are good and bad irons as well as good and bad steels.

There is plenty of good evidence to support this view, and it seems worse than useless,

therefore, for mill men to engage in wordy controversy over the particular merits of their products. The recent researches of several investigators show that internal stresses or strains in a metal, as well as improper treatment resulting in occluded gas and a porous metal with blow holes, are conducive to rapid corrosion. Modern high-speed methods, unless carefully performed, tend to produce a metal in which various substances, which are present either as impurities or are added to produce certain effects, are more or less segregated instead of being thoroughly mixed, and the iron is pounded and rolled into shape and cooled so quickly that the molecules do not have time to adjust themselves and heavy internal strains may be produced. Of course, the remedy for all this is more careful workmanship and adequate annealing. Metal which is strained beyond its elastic limit can be shown to be more easily corroded than metal which has not been strained, and it apparently makes little difference whether these strains are produced during the process of making the part or afterward.

There seems to be no doubt that at least some of the metal produced previous to the

introduction of modern methods (modern as far as speed is concerned) was superior in its resistance to corrosion to the present-day product, although the latter should not be condemned too hastily on this one point alone. Thus, I have seen various iron articles, especially nails, which showed far less rust after an exposure of a hundred years or so, than the modern variety sometimes does in a few weeks.

Another piece, an old flint-lock pistol, was especially interesting. It was found by a friend in a patch of woods in Vermont and had evidently lain there for many years, since a piece of newspaper dated 1796 had been used as wadding in loading it. All the iron parts were rather rough and pitted and covered with rust, but the arm was in surprisingly good shape, considering the conditions to which it had been subjected. The spring, hammer, and trigger were still capable of performing their functions and very little effort was required to put the old weapon in decidedly presentable condition after its extraordinary exposure to the weather.

The old bridge at Newburyport, Mass., has also attracted much attention because after something like a hundred years' exposure to

the elements it shows remarkably little evidence of deterioration.

Going farther back, a number of iron articles have come down to us from ancient times, and perhaps the most noted of these is the famous pillar in the temple of Kutab Minar at Delhi, India. This old shaft, which projects some 30 feet above the surface of the ground, was erected about 900 B. C. Today it shows little trace of rust, although it has had no protective coating other than that which the process of manufacture and the atmosphere itself have formed upon it.

In this connection mention may also be made of what are known as the Ceylon link and the Singhalese chisel, nail and bill hook, all specimens of great antiquity.

To explain how or why these various articles have so successfully withstood the attacks of air and moisture for so many years is not as easy as it might seem, for apparently some of our commonly accepted notions and theories as to what a good iron should and should not be do not hold, or at least are offset by other conditions. For instance, some of the links of the Newburyport bridge have been examined and found to be of very ordinary purity and of a most heterogeneous

structure, segregation of the impurities being decidedly noticeable. The question of any inherent superiority in the iron itself was settled by heating and rolling one of the links into a sheet and exposing it to the weather, when it was found that it corroded quite as readily and extensively as the material of to-day.

Again, tests made on the old relics referred to above show that only in manganese content do they approach modern irons in composition; the phosphorus is from 22 to 60 times and the silicon from 9 to 50 times as high in these as in the present product. From this it would seem that on the score of composition they are in no way superior to our own material, and in addition they contain several per cent of slag and cinder, which are admittedly very undesirable.

The explanation of their good behavior in service is probably found in the fact that the iron from which they were produced was refined, and the objects themselves fashioned slowly and laboriously by hand in a sort of forge. The prolonged heating and slow forging would tend to insure thorough annealing and freedom from strains, while the constant hammering produced a dense skin on the sur-

face, and this was doubtless covered with a more or less heavy coating of scale or oxide which also helped to protect the metal beneath. Thus it seems that the ability of these irons to withstand atmospheric attack is incidental to the method of working, rather than due to greater purity or freedom from segregation, as compared with modern irons. Of course, to apply such methods to the enormous output of iron and steel nowadays would be utterly impossible.

Mention has been made of the impurities in iron, and it may not be out of place to enumerate some of them at this time. All except very highly purified iron contains silicon, sulphur, phosphorus, manganese, and combined carbon, at least in small amounts. In making alloys, chromium, vanadium, tungsten, nickel, copper and several other elements may be added. Iron alloys or combines with practically all the other elements, and is so easily influenced by some of them that oftentimes only a very small percentage is required to alter its character markedly; as a consequence, specification requirements are generally drawn very rigidly.

A good deal of importance has been attached to the influence which sulphur, phos-

phorus, and the other normal constituents of iron are supposed to exert on the process of corrosion, and manganese, in particular, has come in for an unusual amount of condemnation. For example, it is known that it decreases the electrical conductivity of iron, to a certain point; therefore, unless it is uniformly distributed, the electrical conductivity will vary in different parts and on different surfaces, which has an important bearing on the problem in hand, as will be seen later on. Further, it is well known that manganese and sulphur tend to combine when both are present in iron and steel, and the resulting sulphide shows a difference of electrical potential against iron, which is a highly undesirable condition. In general, it may be said that, according to the electrolytic theory, any condition which tends to produce a difference of potential between surrounding parts is bad and will excite or accelerate rapid corrosion.

A detailed discussion of the influence of the various elements, as far as corrosion is concerned, will be taken up later on, but it may be said here that the results of a vast amount of experimental work show that even extremely pure iron corrodes about as readily

as a good, commercial grade of material; therefore the question is apparently not so much what amount of impurities may be present as whether these are thoroughly distributed throughout the metal or segregated here and there in patches.

Before we can discuss some of the theories regarding the formation of rust and thus approach the subject in a scientific manner, however, it will be necessary to review briefly certain chemical and physical facts involved in the process, in order that there may be no misunderstanding of the terms and principles employed. Primarily we will be concerned with the phenomenon of solution.

Water is the great solvent for all forms of matter and there is probably nothing which it does not affect in some way. Most chemical changes take place in water, or in its presence, so it is not only destructive in its action, as we often feel, but also constructive, as new compounds may be formed as well as old ones broken up. When we speak of the solubility of a substance we refer to the ease with which it goes into solution; therefore we say it is insoluble if we find that no appreciable amount has been dissolved. Practically, however, there is almost nothing

which is not dissolved to some extent, so the term is only relative, and there are all degrees of solubility ranging from those cases in which the solvent dissolves but an infinitesimal amount of the material, to those in which it takes more than its own weight of the substance into solution.

This is not the place to discuss why a certain solid does or does not dissolve in a certain liquid, so we will confine ourselves to substances which are easily recognized as soluble in water, that is, dissolve readily in it. When such a body is placed in water it disappears from view more or less rapidly, and its molecules, if it is a compound body, distribute themselves uniformly among the molecules of the solvent. This distribution is produced by a very definite force, known as the ''solution pressure,'' which is exactly analogous to the pressure exerted by a gas confined in a closed vessel. Under such circumstances the gas tends to occupy all the space at its disposal, and therefore produces a certain uniform pressure on all parts of the vessel. If we had steam at a pressure of 100 pounds per square inch in a boiler and wished to introduce more steam into the latter, it is evident that we would have to have

the incoming vapor at a pressure slightly higher than 100 pounds per square inch, in order to overcome the back pressure, as it is called. Again, as a boiler is generating steam and the tension increases, it becomes ever harder for the water to assume the vapor state, against the pressure of the steam already formed.

The same thing happens in the case of solutions. As more and more of the substance dissolves, there is produced a back pressure, known as osmotic pressure. It is evident that when the osmotic and solution pressures are equal, no more of the material will go into solution and a state of equilibrium will result. If any outside influences disturb this equilibrium and lower the osmotic pressure, for example, it is easily seen that more of the substance will pass into solution until equilibrium is again established. Osmotic pressure may be of surprising magnitude, in certain cases, and can be shown by placing a glass tube closed at one end by animal parchment and filled with alcohol, in a glass of water. Alcohol and water have a strong tendency to diffuse or mix, and water can easily pass through the parchment into the tube, but the alcohol cannot; therefore the column

of liquid in the tube will rise, showing an increased pressure. It may be interesting to note that the solution pressure of a very soluble substance, like sugar, is considerable. One investigator found that the pressure in the case of a 6 per cent sugar solution amounted to nearly 60 pounds per square inch.

Coming now to the behavior of substances in solution, we know that if we dissolve salt in water it apparently disappears, but since we realize it must be present in some form we conclude that it has been resolved into extremely fine particles. Experiment has shown that such a solution will conduct a current of electricity and two entirely new substances will make their appearance, one around each electrode, so it is plain that something in the solution is capable of carrying the electricity from one pole to the other, and that in so doing certain changes have taken place. The term "ion" was introduced, therefore, to denote the particle of matter which travels in the solution, along with the electricity, toward the poles. A further distinction is made in that the particle of matter which travels toward the anode or positive pole is called an an-ion, and that which migrates

toward the cathode or negative pole, a cation.

The theory of dissociation holds, at the present time, that when acids, bases, and salts are dissolved in water they break down into ions, which are considered to be atoms or groups of atoms carrying large charges of static electricity. These charges are not apparent in the undissociated molecule, because the positive charges exactly neutralize the negative ones. Thus, hydrochloric acid dissociates into positive hydrogen and negative chlorine ions; sodium hydroxide (caustic soda) forms positive sodium and negative hydroxyl ions; ferrous chloride forms positive ferrous and negative chlorine ions, and so on.

Putting it in the form of a principle, without taking the time to demonstrate it, we may say that the cation of all acids is hydrogen; the anion varies with the acid. Likewise, the anion of all bases is the hydroxyl group (OH); the cation varies with the base, the metal with which it is combined. Since hydrogen is the characteristic ion of all acids, it can be seen that whenever its ions are present, acid properties are exhibited; in like manner, hydroxyl is the characteristic ion of

all bases, and when hydroxyl ions are present basic properties are in evidence. With salts, both the anion and cation vary according to the elements composing the salt. It is not possible to discuss this interesting topic further, but anyone who wishes more information along these lines should consult some good text book on physical chemistry. Perhaps the application of the foregoing to the corrosion of iron may seem a little obscure, so we shall anticipate enough to say that this process is greatly retarded or accelerated by the presence of different ions, therefore some knowledge of their formation and action is necessary.

Another form of breaking down or dissociation, known as hydrolysis, is also of importance in the study of corrosion. If a solution of the carbonate, say, of sodium, potassium, or other strongly basic metal be tested with litmus paper, it will be found to have a strongly alkaline reaction. On the other hand, chromium, bismuth, aluminum and other weak bases tend to form salts which have an acid reaction; some are even too weak to exist. The principle may be deduced, therefore, that a compound formed from a weak acid and a strong base will be alkaline

in reaction, while one formed from a strong acid and a weak base will be acid.

When considering the theory of dissociation it was said that hydrogen ions are the cause of an acid reaction and hydroxyl ions the cause of an alkaline reaction. Conversely, it can be said that an acid reaction denotes the presence of hydrogen ions, while hydroxyl ions are shown by an alkaline reaction. It has just been noted that different ions may exert great influence on the process of corrosion; therefore, when we go into this more deeply later on we should be able to explain, in many cases at least, why certain pigments are stimulators of corrosion, or why they tend to act on the oil in paint films and cause early decay and failure. Basic carbonate of lead—white lead—for example, is so alkaline in its reaction that it saponifies or makes lead soaps of the linseed oil, leading to what is called chalking and deterioration of the paint film.

A further investigation of solutions shows that some will conduct a current of electricity while others will not. A substance which will conduct a current when in solution is called an electrolyte. For example, potassium nitrate, saltpetre, in solution will conduct a

current very readily, but syrup offers a high resistance to its passage. It can be shown that potassium nitrate ionizes highly in solution, which is not true of sugar, and it has been noted previously that when a current is passed through a conducting solution a mechanical movement of the ions takes place toward the electrodes, where they give up their charges and "plate out" in metallic or gaseous form. This may be familiar to the reader as the process of electro-plating. If a solution of zinc sulphate is made to conduct a current, the positive zinc ions proceed to the negative pole, give up their charges, and assume the atomic condition. An equivalent amount of sulphuric acid is set free at the same time at the positive pole. If this is of zinc, as in electro-galvanizing, the acid attacks it and a further quantity of metal is taken into solution. Going a step farther, it is not necessary that an external source of electricity be provided before electrolysis can take place. Strips of two different metals will generate a current when they are put into an electrolyte and the upper ends touched together or joined by wire. This may be explained by saying that the more electro-positive metal shoots positive ions into the solu-

tion and thus leaves itself negatively charged, consequently appearing as the negative pole. It is more or less rapidly disintegrated, while the other is protected. As will be shown later on, this phenomenon plays a very important part in the preservation of iron, especially by zinc coatings.

As everyone knows, all but a few of the elements are capable of combining and forming compounds with the other elements. The capacity of an atom to combine with other atoms is known as its "valence" and varies with the different elements. For instance, one atom of chlorine can combine with only one atom of another element; one atom of zinc can combine with two monovalent atoms, and so on. Sometimes the same element varies in its ability to combine with others; for example, copper combines sometimes with one and sometimes with two atoms of chlorine. Manganese, gold, iron, and many others exhibit this peculiarity, which is thought to be due to the electrical state of the ion. By appropriate means such an element may be made to combine with a larger quantity of another element, if it is in the lower state of oxidation, or to give up a part of the element with which it is combined, if it is in the higher

state.   Passing from a higher to a lower state
of valence is known as "reduction" and from
a lower to a higher state as "oxidation."
Often one of these states is very unstable,
tending to pass into the other under ordinary
circumstances.   Thus iron forms two classes
of compounds, ferrous and ferric, which have
a valence of two and three, respectively, but
the ferrous compounds oxidize very easily to
the ferric state.

If we immerse pure iron in pure water a
certain amount of it will be dissolved, since
iron has a small but definite solution pressure
in water.   It goes into solution as ferrous
hydroxide; therefore, the iron is present as
positive ferrous ions, the hydroxyls taking
the negative charge.   As soon as the ferrous
ions come into contact with the oxygen of the
air they are oxidized to the ferric state.   Fer-
ric hydroxide is insoluble in water, therefore
it precipitates out; and since its influence on
the solution is then at an end, more iron will
dissolve and so the process will be repeated
over and over until all the iron is used up.
Meanwhile the precipitated iron compounds
accumulate and the rust rapidly grows
thicker.

We referred a moment ago to the process

of precipitation and it will be interesting to
consider briefly some of the properties of the
product of this action. Under certain condi-
tions, precipitates may take the form of very
fine crystals and are termed "crystalloids,"
or they may appear in a gummy, gelat-
inous condition and are then called "col-
loids," a word which is derived from the
Greek word meaning glue. There are two
important properties of colloids which should
be carefully noted. The first is their peculiar
propensity to absorb large amounts of liquids
and impurities from the solutions from which
they were precipitated. Since many pig-
ments are first formed as colloidal precipi-
tates, it will be seen that a serious source of
danger is presented as the absorbed impuri-
ties may more than neutralize any inhibitive
qualities of the pigment itself. The second
point of interest is the fact that colloidal
precipitates suspended in an electrolyte be-
have just as ions do, carrying electrical
charges and migrating to the electrodes when
a current is passed. Colloidal ferric hydrox-
ide and all basic hydroxides collect around
the cathode, therefore they may be consid-
ered to have a positive charge. Hydroxides
of an acid nature move toward the anode

and thus have a negative charge. The most likely explanation of this is that a basic hydroxide, for example, would split off negative hydroxyl ions and leave the residue with a positive charge, while an acid hydroxide would split off positive hydrogen ions, leaving the remainder with a negative charge.

The practical significance of these facts is that they help to explain why the surface of a piece of badly rusted iron shows, as everyone has observed, many small but distinct pits or depressions at some places and wart-like growths at others. Under the influence of the electric currents formed during the process of corrosion, the ferric hydroxide is transported from the points having a positive charge, leaving tiny depressions, and deposited at points of negative polarity, thus raising these above the rest of the surface. This feature will be taken up later.

Chapter II

THEORIES OF CORROSION

IN the preceding chapter we considered some of the fundamental principles of physics and chemistry on which the explanation of corrosion is based so that now we are in better condition to undertake the study of this subject itself. Speculation concerning this process has been rife for a great many years and various theories have been put forth from time to time which have endeavored to explain satisfactorily all the observed facts and, incidentally, point the way to a remedy. Some of these theories could not stand rigid investigation and consequently fell by the roadside, but three more or less distinct propositions have gradually been evolved, and practically all students of this subject are adherents of some one of them.

The hydrogen-peroxide theory was based on a scheme of oxidation proposed by a German chemist, Traube. It assumes that when iron, water, and oxygen are in contact, a re-

action takes place in which ferrous oxide (oxide of iron) and hydrogen peroxide are formed. The ferrous oxide then reacts with one-half of the hydrogen peroxide to form a basic or hydrated oxide; rust, an insoluble basic oxide, is the final product. Part of the excess of peroxide then acts on more iron, forming ferrous oxide and water, whereupon more of the peroxide reacts with the iron compound to produce a further quantity of basic oxide, and so the process is repeated indefinitely. Perhaps these relations may be made clearer by the following chemical equations:

$$Fe + O_2 + H_2O = FeO + H_2O_2$$

Iron, Oxygen, Water, Ferrous oxide, Hydrogen peroxide

$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 = Fe_2O_3,H_2O$$

Ferrous oxide, Hydrogen peroxide, Hydrated oxide, Rust

Then,

$$Fe + H_2O_2 = FeO + H_2O$$

Iron, Hydrogen peroxide, Ferrous oxide, Water

$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 = Fe_2O_3,H_2O$$

Ferrous oxide, Hydrogen peroxide, Hydrated oxide, Rust
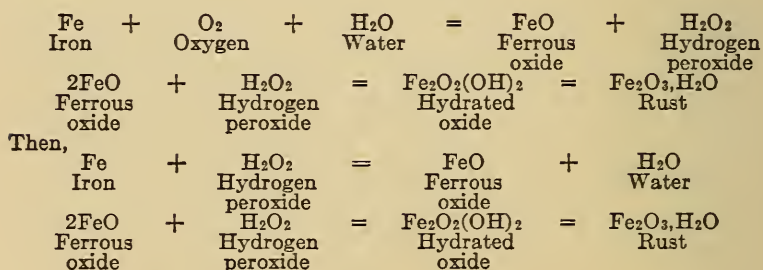
As a whole, this theory has seemed to derive some support from the fact that slight traces of hydrogen peroxide have been detected during the slow oxidation of certain metals. However, the same tests have not shown this substance to be present while iron is rusting.

Another argument which, for a time, seemed to be strong evidence for the theory was the observation that certain oxidizing agents, as chromic acid and its salts, prevent rusting when iron is immersed in water containing them; and hydrogen peroxide is known to be broken up by chromic acid. It has been pointed out, however, that because certain substances destroy hydrogen peroxide, they do not necessarily prevent its formation, a contention which is borne out by analogous reactions with other compounds. A strong argument against the theory is the fact that other oxidizing agents which destroy the peroxide do not act the same as chromic acid and prevent rusting. Altogether, this theory does not seem to be sufficiently in accord with the known facts to serve as a working thesis.

Of the two remaining theories, the carbonic acid and the electrolytic, the former has had the greater number of adherents and until recently has been considered to explain satisfactorily the phenomena of corrosion. As a matter of fact, it does express the truth to a certain degree, as will be shown later. It postulates that rusting is always started by an acid, even one as weak as carbonic suffic-

ing to do this, the iron being first converted into a ferrous salt, with the escape of free hydrogen. Under the influence of oxygen and water the ferrous salt is oxidized to ferric hydroxide (which is insoluble and settles out) at the same time that the carbonic acid which was required to form the ferrous salt is set free. This again attacks the metallic iron with the formation of more ferrous compound which is again decomposed, ferric hydroxide settling out and carbonic acid being set free to attack more iron and thus make the process a continuous one. The action may be shown by these equations:

$$2Fe + 2H_2CO_3 = 2FeCO_3 + 2H_2$$
$$\text{Iron} \quad \text{Carbonic acid} \quad \text{Ferrous carbonate} \quad \text{Hydrogen}$$

$$2FeCO_3 + 5H_2O + O = 2Fe(OH)_3 + 2H_2CO_3$$
$$\text{Ferrous carbonate} \quad \text{Water} \quad \text{Oxygen} \quad \text{Ferric hydroxide} \quad \text{Carbonic acid}$$
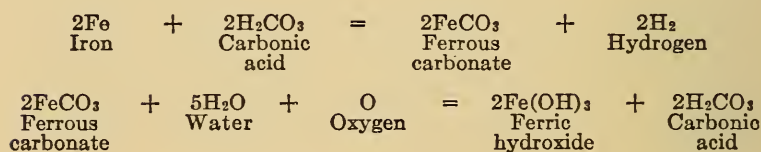
In order to prevent rusting, therefore, all we have to do is to neutralize the acid with an alkali, and those who held this to be the true explanation of the cause of corrosion pointed to the fact that iron does not rust in strongly alkaline solutions. It can be shown, however, that iron rusts very easily in dilute alkaline solutions, so that bit of evidence is thereby weakened.

Various investigators have lined up on both sides of the question and have defended their views with a series of ingenious and painstaking experiments, the object of which was to determine whether or not iron can rust in oxygen and water in the complete absence of carbonic acid. The result of this work seems to show that iron will corrode rapidly in the absence of this substance if oxygen and liquid water are present, and the experiments were so carefully made that no doubt remains that carbonic acid is only a slight factor in the corrosion of iron and that this process can go on very readily without it. In this connection it may be interesting to cite an experiment which Cushman and Gardner describe in their book on this subject. Two Jena glass flasks were nearly filled with freshly distilled water and boiled vigorously one-half hour, at the end of which time bright, polished strips of charcoal iron and steel were slipped into the flasks and the boiling continued a few minutes longer. The flasks were then completely filled with the boiled water and every trace of air removed. No rust appeared on the strips, even when they were kept indefinitely in this boiled water. Pure oxygen was then freed from

every possible trace of carbonic acid and passed into the flasks, whereupon rust formed on the bright pieces in about five minutes and was heavy in an hour. The action seemed to take place in patches having the appearance of a pattern, corresponding to the physical structure of the metal. This experiment was also made using phenolphthalein, a substance which shows the presence of exceedingly small amounts of acid or alkali, and invariably a pink color developed, showing that no carbonic acid was present. This would seem to be good evidence, therefore, that water and oxygen can cause corrosion without the aid of other substances.

The experiment was also tried of substituting pure carbonic-acid gas, perfectly free from oxygen, in place of the pure oxygen used in the above tests. Under these circumstances, no apparent action took place, even after several hours, although no doubt a slight amount of iron went into solution as the carbonate. When pure oxygen was allowed to enter and mingle with the carbonic-acid gas rusting began very shortly, a characteristic blue-green color, which always accompanies the early formation of rust in the presence of carbonic acid, being noticed. In

normal rusting in the air this color is not to be seen.

It can be further shown that, even if it is not possible to remove all traces of carbonic acid from the apparatus used in these experiments, the hydrogen ions which would be given by the dissociation of small amounts of this substance would not be much greater in number than those furnished by the dissociation of pure water. On the whole, it may be said that the carbonic-acid theory expresses a partial truth, in that hydrogen ions must be present before iron can be attacked— a point which will be taken up later.

The electrolytic theory is steadily gaining adherents because it seems to offer a satisfactory explanation for a greater number of observed facts than do any of the others. The modern conception of the reactions which take place between different substances in the presence of water holds that they are accompanied by certain readjustments of the electrical state of the reacting ions, and according to the electrolytic theory iron must go into solution as a ferrous ion before it can be oxidized in the wet way.

When metallic iron is put into a solution of copper sulphate (blue vitriol) the copper

is precipitated in metallic form and the iron
goes into solution, the ions of this taking the
electrical charge of the copper ions. Now
hydrogen is a metal, or at least it behaves
like one, and has a lower solution tension
than iron; therefore if we place a strip of
iron in a solution containing hydrogen ions,
its atoms will assume an electric charge and
it will be dissolved, as it was in the copper
solution, while hydrogen will give up its
charge, changing from the ionic to the atomic
condition and escaping as a gas. Ferrous
salts, especially in solution or freshly precipi-
tated, are rapidly oxidized to the ferric state
by atmospheric oxygen, so that all the elec-
trolytic theory must do is account for the
solution of the iron in the first place.

It has been shown by the careful experi-
ments cited that iron is slightly soluble in
pure water, but as long as no oxygen is per-
mitted to act on the solution no sign of cor-
rosion can be seen. When it is admitted,
however, the red ferric hydroxide soon pre-
cipitates out. So, from the results of these
and other experiments, there can hardly be
any doubt that iron dissolves in pure water
without the aid of other substances.

A little reflection will show that before

iron can rust it must first go into solution, at the same time that hydrogen is set free, and oxygen must be present to oxidize the ferrous salts formed. An exchange of electricity between the reacting ions is therefore demanded and the case may be considered to be one of electrolysis, as the disappearance of a hydrogen ion, as the hydrogen goes off as gas, means the appearance of a ferrous ion somewhere else. Going a step further, it can be seen that corrosion is due to the iron being attacked by hydrogen ions and taken into solution, so we should naturally suppose that anything which increases the concentration of these ions would increase the rapidity of corrosion and, conversely, anything which decreases their concentration would tend to retard or prevent it. And this is precisely the case. It was shown in the preceding chapter that hydrogen is the characteristic ion of acids and hydroxyl that of bases; therefore we should expect acids to stimulate corrosion and alkaline substances to inhibit it, which is in accord with fact.

Taking a bird's-eye view of the process of corrosion as explained by the electrolytic theory, we see that it lines up about as follows. When iron and water are brought to-

gether a certain amount of the metal goes
into solution, since it has a certain solution
pressure—or, to put it a little differently,
water even when very pure is dissociated
slightly into hydrogen and hydroxyl ions, the
former attacking the iron as outlined before.
It can be shown that the solution tension va-
ries at different parts of the surface, this
variation being due to strains and segrega-
tion of impurities; impurities in the solvent
also tend to increase the solution tension.
Therefore, the points where this is greatest
will be positive to those at which it is of les-
ser degree, and a current will flow between
them if there is a conducting medium present.
Remembering that hydrogen acts like a
metal, it is seen that its ions will tend to col-
lect around the negative poles, while the
hydroxyl ions will move toward the positive
poles and try to exchange their static charges
with the iron, so that the latter will go into
solution and the hydrogen escape as a gas.
If the hydrogen ions are in sufficient concen-
tration, that is, if an acid is present, this ex-
change of charges takes place very rapidly
and the iron is quickly dissolved. Under or-
dinary conditions, however, the action pro-
ceeds much more slowly as the concentration

of the ions is comparatively low. Iron goes into solution, nevertheless, as can be shown by means to be described shortly, and for every ferrous ion which is formed a hydroxyl ion must be formed also and appear elsewhere. The oxygen of the air now acts on the ferrous salts and changes them into the ferric state, in which form they precipitate out as the familiar red rust, and so the process is repeated indefinitely.

Mention has already been made of so-called indicators, substances which show by a change of color the presence of very small quantities of acids or alkalis, and these are employed to show the positive and negative poles. Through the work of several investigators the reagent known as ferroxyl was developed. It consists essentially of phenolphthalein, which shows the negative poles, and potassium ferricyanide, which indicates the positive poles, in a solution of gelatin or agar. It has proved to be a very valuable help in these lines of study and has widened our knowledge considerably.

Nearly everyone has observed that not all pieces of iron rust in the same way. Some are covered more or less evenly with a coating of rust which is of fairly uniform thick-

ness; others are deeply pitted in some places,
while adjacent parts of the surface may show
far less corrosion than might be expected.
Without the aid of the ferroxyl test it is diffi-
cult to explain just why these things should
be.

When a strip of iron is properly mounted
in this reagent, various parts of the surface
develop either a red or a blue color after a
few hours, thus showing where the positive
and negative poles are, which is equivalent
to saying where the iron is being attacked by
hydrogen ions and where it is being protected
by the presence of the hydroxyl ions. Often
these poles reverse and a positive pole be-
comes negative, or *vice versa;* in fact, this
reversal may be repeated several times. In
this connection, perhaps it would be best to
describe the results of such a test made by
Cushman and Gardner and given in their
book, to which reference has already been
made. A strip of steel was placed in ferroxyl
and carefully observed.

When the colors first developed two dark blue
nodes formed at the opposite ends of the test piece,
with a large pink area at the centre, where for a time
the metal remained quite bright. Very slowly, how-
ever, the poles changed and the pink central area

disappeared and gave way to a large blue node which enveloped three-quarters of the test piece, with a small opposed pinkish spot. Again and again a reversal and change of poles took place and at least five such changes could be observed. As a result of this action the metal strip was rapidly covered over its entire surface with the same superficial, loosely adherent coating of hydroxide which is obtained in many cases when certain samples of iron and steel are allowed to rust under a layer of water. It is presumable that as the surface of the metal is eaten into by the solution of the iron at the positive poles, a new condition of equilibrium occurs, resulting in changes and even reversal of the positive and negative nodes. This would indicate that in the case of metals which suffer from local action or pitting, the segregation conditions are of a different nature from those which exist in the case of metals which rust more evenly. A rough analogy may be drawn by imagining an imperfect mixture of black and white sand, the respective grains of which may lie in streaks, spots and layers, or may tend to arrange themselves in some more or less uniform relation to each other. The best demonstration that the rusting and corrosion of iron and steel in all its forms is essentially an electrolytic phenomenon is afforded by the fact that it has not as yet been possible to find a specimen of such purity that no trace of positive or negative nodes will be formed in the ferroxyl indicator.

Having now outlined the principle of the electrolytic theory, it will be instructive to consider it in its practical relation to the problems at hand and see if it agrees with observed facts. It was stated in the preced-

ing chapter that colloidal ferric hydroxide be-
haves like an ion and travels to the negative
pole under the influence of a current, and
since a current must flow, according to the
theory, when iron corrodes we should expect
the ferric hydroxide to be affected. Now
anyone who will examine, under a glass, a
piece of badly rusted iron will often find a
place where the rust is piled up like a cone
and surrounded by a ring which has been
eaten into the metal, or perhaps, the metal
has been dissolved out of a certain spot and
the ferric hydroxide piled up all around it,
like a crater. It can be assumed, therefore,
that the cone marks a point of negative po-
larity, while in the other case the depression
in the centre of the ring is positive.

It will be evident from what has gone be-
fore that anything which tends to prevent the
formation or flow of current also lessens the
tendency to corrosion, a point which will be
touched upon later in connection with insulat-
ing and conducting pigments. So we should
expect that very pure iron would be more re-
sistant than that which is impure, and this is
found to be true, at least in large measure.
As evidence of the truth of this general prop-
osition, it has been shown that if two nails,

say, are placed in water or ferroxyl and one of them is connected to a piece of platinum wire while the other is left free, the former will corrode much more rapidly than the other. This may be explained by saying that the hydrogen which is set free can deposit on the wire and thus be removed from the scene of action much faster than in the other case.

In a similar way, when two pieces of iron, one of which is attached to a piece of zinc, are immersed together in water or some electrolyte, the free strip of iron will rapidly decay, while the piece connected to the zinc will be protected, although the latter slowly dissolves. Zinc is electro-positive to iron; therefore a current flows from it to the iron, causing hydrogen to deposit on the latter and thus protecting it. (Gaseous or atomic hydrogen must not be confused with that which is in the ionic state. It has been shown that the latter attacks iron and takes it into solution, but gaseous hydrogen, settling out in the form of bubbles on the iron, will make a thin film of gas which is a good protective from further action. This is illustrated by the "polarizing" of an ordinary sal ammoniac battery.)

These examples help to show why zinc, as applied in galvanized coatings, is such a good protector of iron. Through its impermeability it keeps the iron away from harmful influences as long as possible; then when moisture and air do reach it, an electrolysis is set up which effectually protects it until most of the zinc is destroyed.

If a piece of iron oxide is substituted for the zinc in the foregoing experiment, it is found that the free piece of iron corrodes much more slowly than the one in contact with the oxide, showing that this must be electro-negative to the iron, therefore hastening its corrosion. The coupling together of two parts, one of which is electro-positive to the other, with the result that the corrosion of the former is much accelerated, brings to mind a possibility which is ever present in iron structures: that is, through some cause or other one member may be positive or negative to the others and, unless proper precautions are taken, all the conditions for early decay of some of the members are present. At least one instance of such action has been recorded, when certain members of some structural iron-work were almost entirely destroyed, while others were in practically per-

fect shape. There seems to be no doubt that the parts which were destroyed were electro-positive to the others. The obvious remedy for such a condition is to assemble only parts having practically the same chemical composition and treatment and, further, to insulate them from each other as far as possible by coating all contact surfaces with red lead in oil.

Mention has been made of the fact that stresses and strains, whether produced during the process of manufacture or afterward, as well as improper heat treatment and segregation of impurities, are great factors in determining the extent and magnitude of the differences of electrical potential which will be present. To these may be added the effect of pickling in acids, a process which is widely used in preparing metal parts for finishing. Investigation has shown that iron which has been pickled may contain considerable quantities of hydrogen, being made markedly harder thereby, and is easily oxidized. In the experience of the writer, pickling is distinctly bad and should be avoided whenever possible, especially in cases where even slight traces of rust are objectionable. Of course, this applies only to painted or japanned

work, as all electro-plating processes demand some such preparation of the parts and bad results do not seem to follow. It is interesting to note, however, that electrolytic iron which contains a large amount of hydrogen is corroded with difficulty. Other considerations lead to the belief that the hydrogen in pickled iron is not present in very stable combination, while that in electrolytic iron forms a true alloy, which may be much more resistant than iron alone.

Coming now to iron which is actually in service in buildings and similar structures, it is found that this often behaves in a rather unexpected manner as regards its tendency toward corrosion. Those parts immersed in a few inches of water may corrode with great rapidity, while other parts placed a considerable distance under the surface will remain in practically perfect shape almost indefinitely. Similar conditions are found in parts buried in the ground. The explanation is to be found in the fact that both water and oxygen are necessary to produce corrosion. If, therefore, iron parts are immersed in water or buried in the ground to a depth greater than that to which oxygen can penetrate, they will be preserved because the con-

ditions for corrosion have not been attained. The literature contains many examples of such action and it is impossible to do more than refer to it here.

Somewhat along the same line is the observation that iron in swiftly moving water does not corrode as rapidly as that in more quiet situations, dissolved oxygen being present in both cases. It is a matter of record that pipe lines corrode from the outside rather than from the inside. It may be conjectured, on the basis of the electrolytic theory, that under these constantly changing conditions the nodes or points having a different potential are changed too frequently for serious rusting in one spot to take place.

A little observation will show that "busy" iron, as it has been termed, does not rust as readily as that which is not in service. Perhaps steel rails are the commonest example of this and it is well known that little or no corrosion is seen in lines on which the traffic is fast and heavy. Sang thinks that this may be explained by the "assumption that vibration causes a shedding of the rust as soon as it is formed on the spots not protected by mill scale and there is, therefore, no accelera-

tion of the action due to the accumulation of
spongy and electro-negative rust.''

It is apparent that corrosion does not al-
ways take place with the same rapidity or
uniformity; therefore certain processes or
treatments may render iron less susceptible
to decay, and the word ''inhibitive'' has been
used by Cushman, in the sense of limiting or
checking it. If a piece of iron is dipped into
concentrated nitric acid for a short time, it
is rendered passive; that is, it will stand a
much longer exposure to adverse conditions
than ordinary iron, and it precipitates cop-
per from its solutions only very slowly. Just
what the action is may be open to question,
but apparently there is a lowering of the
electrical potential. This state is the abnor-
mal or unstable one, however, so the piece
gradually returns to the normal condition
and increasing corrosion takes place. Chro-
mic acid and its salts also act like nitric acid
and can produce the passive state. Work has
been done in the way of putting these facts to
practical use, and it may be that some effi-
cient process will be discovered whereby iron
can be made much more resistant. Other
ways of inducing passivity are by electrolyz-
ing in distilled water or caustic potash, some

investigators using weak and others heavy currents.

We have seen that hydrogen ions are stimulators of corrosion and hydroxyl ions are inhibitors, so strong alkalis are perfect rust preventives. The explanation is that neither hydrogen ions nor hydroxyl ions can exist in the same solution in excess, in relation to each other. Now, any condition which tends to further the escape of gaseous hydrogen and thus eliminate its polarizing and damping effect on corrosion acts as an aid to this process, so it has been found that under certain conditions a paint film may actually increase, rather than diminish it. Walker mentions a case where the application of a high-grade varnish to the inside of tinned-iron fruit cans led to highly stimulated corrosion. This was explained on the basis that the coating, which was probably perfect when made, was ruptured and destroyed at certain points during the process of manufacture of the cans. When the fruit juices set up electrolytic action the varnish acted as a depolarizer and combined with the hydrogen, thus stimulating corrosion to the point of destruction. Thus it is that a film of linseed oil alone may encourage rather than prevent decay, since

it is porous and unsaturated chemically. It has often been the custom in the past to coat structural steel work with linseed oil before it left the shop, and many cases of rapid corrosion can be traced to this practice. Direct experiments have shown that iron parts which have been coated with linseed oil and the film then destroyed at certain spots by abrasion, corrode much faster than ordinarily. This is probably due to the fact that the film of oil absorbs the hydrogen as fast as it is formed and thus acts as a depolarizer. If pigments are mixed with the oil, however, it loses this power to a great extent. A paint, therefore, in order to accomplish the purpose for which it was designed must be free from voids and of such a character that it will not act as a depolarizer.

Another source of corrosion which must not be lost sight of is in wounds, indentations, and general roughness of the surface. Such peculiarities are almost always electro-positive to the adjacent parts and deep pitting is produced. For this reason razors and other articles which have a high polish will, with the most ordinary care, resist corrosion and remain in good condition for many years, long after a rough piece would be destroyed.

It seems to be a principle, therefore, that the possession of a uniform surface, from the standpoint of chemical composition and freedom from strains as well as the removal of all irregularities and the production of a more or less high polish, tends to make the part much less susceptible to the attack of corrosive influences than is the case with less carefully made articles.

PROTECTIVE MEASURES

AFTER a working knowledge of the causes and general nature of corrosion is obtained, the next step is to apply it toward the protection of iron and steel from those malignant influences so familiar to every engineer. Since these materials can not stand exposure very long, while unprotected, it is evident that they must be covered with some substance or preparation which will exclude moisture and air and itself be impervious to the action of these agents. We may say that this represents the ideal and that in practice it is almost, if not absolutely, impossible to attain these conditions completely, although improvements are constantly being made in consequence of the great amount of work which is being done along these lines.

Roughly, the problem of the protection of iron and steel falls into three classes: 1. Protection by a coating of oxide produced on the surface by various processes. 2. Protect-

ive coatings of other metals. 3. Protective coatings formed by paints and similar materials.

Many years ago Lavoisier, a famous French chemist, noted the formation of mill scale, which is mostly the magnetic oxide of iron, and commented on its stability and impervious character. Later on Faraday described the protective action of the oxide formed in the tubes of a steam superheater. Another observer discovered its formation when iron is acted on by highly heated air, and Prof. Barff, of London, became interested in this oxide as a protective measure through his observations of a pipe carrying superheated steam. His process, which was first made known in 1876, consisted in heating the parts to 1,000 degrees C. and passing steam superheated to 538 degrees C. over them.

A Mr. Bower and his son tried using air instead of steam, but were unable to obtain the desired results until they employed producer gas to reduce the red oxide formed by heating the parts in air. The air treatment lasted forty minutes and the gas treatment twenty minutes, these being repeated alternately four to eight times. Finally they pur-

chased the Barff patent and the Bower-Barff process was originated.

In this process the parts to be treated are heated to nearly 900 degrees C. in a closed retort; superheated steam is then led in for twenty minutes and a coating consisting of a mixture of the black and red oxides of iron is formed. Producer gas is now substituted for the steam and passed in for about the same length of time. If the coating thus formed is not sufficiently thick, these operations are repeated as often as necessary. Paraffine or some other oil is afterward applied to the parts, whereby a fine black color is obtained and additional protection afforded.

As regards cost, this process is expensive, the price ranging from $5 to $20 per ton, but it can be applied to almost anything which will not be injured by the heat and is small enough to be placed in the furnace, and it affords very efficient protection, especially against sea-water, acid fumes, and like influences. Paints and enamels can be applied and adhere strongly. Parts given this treatment will stand almost any degree of heat without injury, but they may not be bent or machined. Of course, the process is not applicable to tools or tempered pieces. Also,

the parts are enlarged slightly so that those which must maintain close limits on dimensions should not be given this treatment.

An improvement introduced later into American practice, known as the Wells process, consists in finishing the work at one operation, by using steam and producer gas together instead of applying them alternately.

The Gesner process, which is a modification of the preceding, came into use a few years later. The coating is said to be a compound of hydrogen, iron, and carbon, and has less tendency to scale. Analyses have shown that not less than 2 per cent of hydrogen is present. The method of application consists in keeping the parts in the coating retort at a temperature of about 600 degrees C. for twenty minutes, then allowing steam at low pressure to act at intervals for thirty-five minutes. It is passed through a red-hot pipe in the bottom of the retort and thus is partially decomposed into hydrogen and oxygen. After the steam treatment, a small quantity of naphtha or other hydrocarbon is poured in and allowed to act for fifteen minutes, whereby any red oxide is reduced and the surface carbonated.

A variety of work has been finished by this process, apparently at a somewhat lower cost than for Bower-Barffing. It is also claimed to have an advantage over the latter process in that the much lower heat does not burn or warp the parts and that little or no increase in size takes place.

Perhaps mention should also be made of the Dewees-Wood process which was almost identical with that of Gesner and preceded it. In this, sheet iron was subjected to the action of hydrocarbon vapors, or gas, and superheated steam in a closed, heated chamber.

The Bradley process was patented in 1908 and is similar in principle to the last two. In carrying it out, the parts are prepared by tumbling, pickling, or sand-blasting, preferably the latter, and heated to a low red in a muffle, hydrogen gas being passed in. This is followed later by small quantities of gasolene which improves the color of the coating. The articles are left in the furnace for an hour, or until a sufficiently heavy coating of the oxide is produced, after which they are taken out, allowed to cool, and treated with linseed oil or paraffine.

The Bontempi process is another recent

modification or improvement on the original Bower-Barff method. It consists in heating the article as in the Bradley process and then passing in steam and the fumes of zinc or some heavy hydrocarbon as tar or pitch. A new patent has been recently granted covering the use of certain substances which are claimed to further the formation of the black oxide. A uniform finish of a deep black color is obtained, which is said to resist corrosion indefinitely.

Among the several methods which have been used for producing a black oxide coating by the use of moderate heat, that of Buffington may be mentioned. Briefly, it consists in melting manganese dioxide and potassium nitrate (saltpetre) in an iron pot, immersing the cold parts in the mixture for a few moments, then hanging them over the pot in the fumes and finally putting them in boiling water to cool. A fine blue to bronze color is produced.

In about the same way, films of sulphide or phosphide of iron, produced by subjecting the metal to the vapors of these elements at high temperatures in the absence of air, have also been tried, but have not attained to any very extended use.

Heat-bluing, which is familiar to every one, is applied to watch and clock hands, buttons, buckles, and a large variety of steel articles, and gives a finish of a pleasing blue or black color, which is not, however, so very resistant to corrosion. It is produced in several ways, such as dipping the parts in a bath of molten saltpetre, heating them on an iron plate in the air, or tumbling them in a sheet-iron barrel heated by a gas flame. Revolvers and similar parts are very often given a fine blue finish by heating in charcoal.

One of the best and simplest methods of producing a protective black coating is of rather recent origin, and is known as Coslettizing, from the name of the discoverer, Coslett. In this process the parts are first cleaned by pickling or sand-blasting, then immersed in a boiling water solution of phosphoric acid in which iron or zinc filings are placed. They are left in this for a period varying from one-half hour to three hours, depending on the nature of the work or the thickness of the coating desired. A very slight amount of the surface of the article treated is converted into certain phosphates of iron, but most of the coating comes from the solution itself. One advantage of this

method is that it can be applied to small and delicate parts, tempered pieces, edged tools, and so on. Typewriter manufacturers and others who are using it claim that it retards corrosion to a remarkable degree, especially on articles which are in use in the tropics and other places where unusually good protection is required.

In summing up all the above processes, it may be said that Bower-Barffing or any other procedure which gives a heavy coating consisting essentially of the magnetic oxide of iron will afford a durable, efficient finish. It is not absolutely rust-proof, as experience shows that tiny rust spots will generally develop in the course of time. Under extremely bad conditions these appear sooner and doubtless the finish would go to pieces eventually; but although this coating is strongly electro-negative to iron, a circumstance which we should think would tend to accelerate corrosion rapidly when it is once injured, the breaking down is very slow. Perhaps the perfect adherence of the oxide allows the iron to rust only at the exposed places, so that, although it may pit deeply, it is not so noticeable as though it were more extensive. As noted, however, those methods which em-

ploy high temperatures are not applicable to all classes of parts.

Coslettizing appears to be the best of those processes employing low degrees of heat, and it can be applied to practically any iron or steel article, giving it a durable finish. It is not very complicated or expensive, although the cost is increased through the fact that it is a patented process; therefore a royalty must be paid.

Lastly, those methods which produce merely a darkening of the surface ordinarily do not afford much protection from rust, especially on parts exposed to high humidity. They have their place, however, and when used in conjunction with lacquers or like materials may be very useful in producing a fairly good finish.

Coming now to those processes which deposit another metal or alloy on the surface of iron, for the purpose of protecting it, it is found that those involving the use of zinc in some manner are by far the most important. Several factors tend to make this true, but we may mention the comparative cheapness of zinc and the fact that it is peculiarly suited to this work, since it is the most electro-positive to iron, as has been mentioned,

of all the metals which can be used practically for such purposes.

Unlike most metals, zinc may be applied to iron objects in three widely different ways: by dipping them in the molten metal; by depositing it electrolytically from a plating bath; and by the vapor or Sherardizing process. All these methods are widely used, and each has advantages which may especially commend it in certain cases.

In the hot or dip method, the parts are cleaned by pickling, generally dipped in some acid flux, and then immersed in a bath of molten zinc. Sal-ammoniac or other fluxing agent is used in addition to insure the clean surface requisite for perfect adherence of the coating. After the parts have become thoroughly heated and covered with the zinc, they are withdrawn and the excess of metal is shaken or wiped off, depending on their shape.

At first sight it would seem that a very pure coating of zinc is thus produced, but a little consideration will show that such is not the case. In the first place, the zinc bath is not strictly pure, but generally contains a fairly considerable amount of impurities in the shape of other metals, with perhaps slight

quantities of dissolved oxides or oxy-chlo-
rides. Iron, too, is more or less attacked by
molten zinc, so the galvanizing kettle and the
parts themselves contribute a good deal of
iron. After the iron content reaches a cer-
tain point a definite alloy of iron and zinc
settles out, and to prevent it from adhering
and becoming burned onto the bottom of the
kettle it is the practise of many foremen to
add lead to the bath. This melts and, being
heavier than either the zinc or the alloy, set-
tles to the bottom and everything else rests
on top of it. The removal of the alloy, there-
fore, is not difficult and is done at regular in-
tervals. In addition to the foreign sub-
stances above mentioned, many galvanizers
add a small amount of aluminum or tin to aid
in the production of a smoother and better
looking deposit.

It is easily seen, therefore, that the coating
actually produced is a mixture of zinc with
a number of other metals, and perhaps some
actively corrosive bodies derived from the
fluxes. The resulting alloy is very easily at-
tacked by acids, due, no doubt, to the electro-
lytic action set up between the various met-
als. According to some authorities the solu-
tion tension of zinc alloy with iron and

other impurities is greater than that of the pure metal. When a hot galvanized part is exposed to adverse conditions, therefore, it is plain that unexpectedly severe corrosion may take place. A good deal of work is being done to improve the quality of hot galvanized coatings, in the way of employing harmless fluxes and keeping the zinc as pure as possible, so it is likely that much progress will be made, although the very nature of the process is such that a very pure coating can not be produced, at least commercially. Nevertheless, this process is used very widely and enormous amounts of iron are finished by it.

In using galvanized or other material which has been given a protective finish, it is necessary to have some means of determining the probable efficiency of the coating as a preventive of rust, and this is done indirectly by measuring its weight and thickness. For anyone who has access to a good balance and a few chemicals, perhaps the simplest way is to clean and weigh a small piece of the material, and then boil it in strong caustic soda until the zinc is all removed. The piece is then washed, dried, and weighed again. Subtracting this weight from the former one

gives the weight of zinc present, and by divid-
ing it by the area of the part in square inches
the result can be expressed as milligrams per
square inches or ounces per square foot. It
is not always practical or possible, however,
to inspect material in this way, so another
method known as the Preece test is in wide
use.

This depends on the fact that zinc, when
dipped into a strong solution of a copper salt,
is dissolved and takes the place of the copper,
which appears in metallic form. Iron does
the same thing as the zinc, but much more
slowly, so that the copper deposit formed on
the zinc is very coarse and easily removed
while that on the iron is more or less hard
and bright. Putting these together, when a
galvanized piece is dipped in copper-sulphate
solution, the copper first deposited is easily
wiped off, but as soon as the zinc is all gone
the copper plates out on the iron, this point
being determined by the difference in ap-
pearance and behavior of the coating. Prac-
tically, it is sometimes a little difficult to tell
just when all of the zinc is removed; also
there are many factors which may work to
impair the value of the results obtained, so
exact directions have been drawn up cover-

ing the application of the test and the means by which the critical point may be recognized. Thus there is, ordinarily, a good degree of uniformity in the manner of using it. For example, the American Steel and Wire Co. directs that the copper solution shall be neutralized by an excess of pure copper oxide, it shall be filtered before using, and shall have a specific gravity of 1.186 at 65 degrees F.

Samples must be thoroughly cleaned of all grease and dirt and the temperature of the solution must be not lower than 65 degrees F. nor more than 70 degrees F. In making the test the carefully prepared samples are immersed in the fresh solution for exactly one minute. They are then taken out, rinsed in water, and wiped with clean cotton waste, after which they are immersed again for exactly one minute, washed and dried. If the material is required to stand more than two dips, the process is repeated the requisite number of times; then the parts are carefully examined to see if there are any traces of bright copper. If no deposit appears, the parts are considered to have passed the test.

Although this procedure finds wide application, there are several disadvantages or

faults in it, to which attention has been called by investigators. These will be referred to later, after the other methods of producing zinc coatings have been considered, inasmuch as this test has been applied to all these indiscriminately.

It is only within comparatively recent years that it has been possible to obtain a good deposit of zinc electrolytically, on a commercial scale. A great deal of work has been done along these lines, however, so that we are now able to produce very fair coatings, although there is still plenty of room for improvement. In brief, the process consists in immersing the carefully pickled and cleaned parts in a solution composed essentially of zinc sulphate, with a very slight amount of free sulphuric acid. Various organic substances are also added to assist in the production of a smooth, dense deposit. There is a large number of formulæ for these baths, many of which are patented or secret. The plating time varies from twenty minutes to an hour or more, depending on the current density, the weight of deposit required, and so on. Some of the solutions permit the use of current densities as high as fifty amperes per square foot, which is much higher than

was possible when the process first came into use. After the plating period is over, the parts which have been plated are washed in water and dried.

The coating which is produced is of great purity; therefore, it would seem to be superior, in this respect at least, to that given by hot galvanizing. When properly carried out, a very smooth, uniform deposit is applied, so this method is applicable in many cases, as with small parts, where the hot process would clog up small holes or threads and prove generally unsatisfactory. It also possesses the great advantage of very easy control—that is, a coating of definite weight can be produced at will.

On the other hand, the deposit is more or less porous, depending on the conditions under which it is made, and certain impurities may be included which will become active stimulators of corrosion. As far as protection is concerned, there does not seem to be much to choose between the hot dip and electro methods, when testing parts of the same weight of deposit.

As before, the actual weight of zinc per unit area may be determined by stripping in caustic soda, weighing the parts before

and after stripping, and dividing the difference in weight by the area of the part.

In testing electro-galvanized work to see if the coating is of the desired weight, samples are often suspended in distilled water through which air is bubbled, the time required for the first sign of rust to appear being carefully noted. Under such conditions the zinc is converted to the hydroxide or basic carbonate and settles to the bottom of the vessel, exposing the iron. In making the test it is important that certain definite conditions be always maintained, especially as regards the rate at which the air is passed, if comparative results are to be obtained. In passing, it may be said that the value of such an acceleration test, as a measure of the efficiency of a coating in protecting iron from corrosion, may be a doubtful quantity but it does roughly indicate the weight of the coating. The Preece test is also applied to electro-galvanized work, and when properly carried out should be of great value in determining the quality of such a finish.

Sherardizing was developed by Sherard Cowper-Coles, although some of the fundamental facts regarding it have been known for a long time. In this process the thor-

oughly cleaned parts are placed in an iron drum with a quantity of finely powdered zinc, which generally contains a considerable amount of zinc oxide. This drum is then placed in a gas-fired or electrically heated furnace and brought to a temperature of about 800 degrees F. which is maintained for a varying length of time, depending on the thickness of coating desired. On the average a furnace will turn out two charges a day. When the drums are sufficiently cool they are emptied over a grid or screen so that the zinc dust falls through and collects in bins, to be used again.

One great advantage of this process is the fact that the zinc coating is applied very evenly and uniformly over all surfaces accessible to the powder. In this respect it is superior to the methods previously considered, especially the electrolytic, with which difficulty is experienced in getting the zinc to deposit in inner corners and recesses. The size of the parts is increased very slightly by this treatment, but perhaps the main action is one of alloying with the iron rather than depositing zinc on the surface. Dr. Walker says that a polished and etched specimen of Sherardized iron presents a relatively

complex structure. The zinc penetrates the
iron with the formation of deep layers of
two alloys B and C, the latter being richer
in iron than the other. Imposed on B there
are a number of more or less unknown alloys
containing varying amounts of zinc and iron.
Upon the surface there is generally a layer
of relatively pure zinc, although frequently
the process is carried to the point where only
a deep layer of alloys is formed. When ex-
amined under a microscope this alloy is seen
to be covered with cracks or fissures, as
though it had contracted in forming. The
claim is made that even if the outside coat-
ing, which is rather brittle, is removed by
blows or rough usage, the part will still be
protected by the deeper zinc-iron alloys and
will not rust, and practical experience seems
to bear this out. Further, if a deep notch
is filed in a piece of Sherardized work and
the latter is then exposed to the weather or
placed in aerated water, rust will form in
the notch and fill it up completely, then stop.
It apparently can not crawl or loosen the
surrounding coating.

When parts finished by this process are
exposed to the weather or immersed in water,
a yellowish-brown color which may easily be

mistaken for rust develops. This is called
the curing color and is probably caused by
the corrosion of part of the iron in some of
the alloys. At any rate the surface rapidly
turns darker and soon becomes almost black,
from the formation of the magnetic oxide
which is in itself a good protector. On con-
tinued immersion a few weak spots will gen-
erally show up and tiny rust spots form, but
as remarked, these do not spread and for
all practical purposes may be disregarded.
Altogether, the work produced by this method
seems to be as nearly rust-proof and durable
as can be produced by commercial means at
the present time. The fact that it is adapted
to the finishing of both large and small parts,
even those having threads, as screws or pipe,
greatly increases its applicability and it is
being used very widely.

In the ''molten zinc'' process the parts are
placed in a hollow drum which is placed in-
side a larger one. The zinc is heated to the
volatilizing temperature, while hydrogen or
other reducing gas is forced in to prevent
it from oxidizing, and it combines with the
iron, producing about the same results as
Sherardizing. Aside from its use as a means
of affording protection, this method is also

capable of application in decorative work. It is possible to get very beautiful effects by forming alloys with other metals—for example, the production of a brass design on a copper background.

Another procedure, of which only the barest mention can be made, has been developed for finishing wire. It consists in passing a heavy current through the wire, thereby heating it to redness, and drawing it through a mixture of crushed coal and zinc oxide in a furnace. The heat reduces the oxide to the metal, which then alloys with the iron of the wire, forming a coating similar to Sherardizing. Whether or not this process will come into very extended use remains to be seen.

Some little reference has already been made to the Preece test for galvanized work. As a whole it has been objected to on the ground that it assumes that the zinc is removed in direct proportion to the time of immersion and that it really determines the thickness of the coating at its thinnest part. When applied to electro-galvanized or hot dipped work it is a fairly satisfactory means of indicating the thickness and uniformity of the coating, and meets commercial require-

ments of speed and reliability. When applied to Sherardized material, however, it is the opinion of many investigators that very misleading results may be obtained, in spite of the fact that some manufacturers are using it. The trouble apparently is that some of the zinc-iron alloys are indicated as iron, while in reality they have very good protective powers. Perhaps if carried out under very definite conditions and making certain allowances it would prove of value as a ready test, but there are other means of determining the quality of the coating and these are much more accurate, though longer. A very good way is to strip a piece in caustic soda, as described before. Immersion in water is also a reliable means of testing all such coatings. One of the largest producers of Sherardized material in the country is said to test all of its product by subjecting samples to a strong salt-water spray for something like sixty hours.

It should be remembered that all the foregoing methods of testing in which the weight of the deposit is determined do not give much information regarding the freedom from pores. Walker therefore devised a scheme of testing electro- and hot-galvanized ware

for pinholes in the coating by immersing the part in strong, hot caustic soda. Any such imperfections will then be revealed by the formation of streams of small gas bubbles.

Short and simple tests of quality are a necessity and are of real value when rightly used, but the best method of all is by actual exposure to the weather. It requires considerable time to obtain definite results, but when it is possible to do this it is generally worth the time and trouble, as it decides impartially and unmistakably between various finishes or different samples of the same finish.

Of the other metallic coatings produced by electro-plating, perhaps copper and nickel are the most familiar. These are applied both for decorative purposes and to afford protection from corrosion, and are used very widely for finishing an infinite variety of small and medium sized parts, although there are certain disadvantages connected with the use of such coatings. The processes for producing them are rather expensive and call for a high degree of skill; to be really effective under bad conditions a heavy deposit is required, and even then there is a decided tendency to wear away, especially on edges, if

the parts are subjected to much handling. For many purposes, however, no better methods of protection have been devised.

Copper is deposited from two kinds of baths, acid and cyanide. The former is essentially a solution of copper sulphate with a small amount of free sulphuric acid, and is used for plating on any metal which is not attacked by dilute sulphuric acid. Iron, for example, can not be plated in it because it reduces a copper solution, as we have seen, and is itself dissolved by the acid, so the copper cannot adhere to it and the cyanide solution must be resorted to. This is made by dissolving basic copper carbonate in a slight excess of potassium cyanide. It does not attack iron or other metals to any extent and rapidly produces a fine deposit.

Nickel solutions are generally made from nickel sulphate; some platers use the double nickel-ammonium salt, a small amount of free acid being present in both cases. Boric acid is added to brighten the deposit.

Among the metallic coatings produced in other ways, mention may be made of copper-clad steel, which seems to be finding a considerable field of usefulness, perhaps especially in the form of wire. Space does not

permit a description of the process beyond
saying that the copper is applied in one of
two ways, by alloying or by welding. In the
former the copper is in the plastic state,
while in the other it is molten. Copper is
very resistant to atmospheric influences, and
exposure tests of copper-clad wire have
shown it to be practically unchanged after
long periods.

We should naturally expect that the con-
tact of steel with copper would cause the
former to corrode very rapidly, but this
does not seem to be borne out by experiment
and it has been conjectured that after a cer-
tain amount of rust has formed a thin film of
copper oxide mixed with copper is deposited
between the iron oxide and the unattacked
iron and that this acts as a preservative coat.
Altogether it would seem that such copper
and iron combinations should come into wide
use, especially as the former metal is not
destroyed by exposure to moisture and air as
is zinc.

Lead has been used to some extent, and
the Lohmannizing process, which is perhaps
the best known of these, is said to consist
in the immersion of the parts in a bath of
molten pure lead or lead alloys, the secret

being in the use of the proper fluxes. While an alloy of lead and tin is used in the manufacture of terne plate, it is somewhat doubtful if the use of pure lead in this way will come to be very extensive.

Another procedure, which differs considerably from any of those so far discussed and presents some novel features, is that known as the Schoop process, wherein some metal is sprayed by means of an air blast onto the parts which it is desired to protect. The apparatus for doing this is more simple than might be supposed and consists of a sort of pistol, in appearance not unlike an automatic revolver, having three hose leads, through which are conducted oxygen, hydrogen, and compressed air. Inside the pistol the two gases are burned in a burner tube concentric to the air nozzle.

Metal is supplied in the form of a wire, which is drawn in by a suitable feeding device actuated by a small air turbine in the body of the pistol. When the wire reaches the flame zone the intensely hot oxygen-hydrogen flame instantly melts it, while at the same time a strong blast of air issues from the nozzle and blows the molten metal into a cloud or spray, so that it is discharged

from the pistol with a velocity said to be approximately 3,000 feet per second.

It might appear at first sight that the metal would reach its mark in a molten state, but this does not seem to be the case since a few inches from the nozzle it is of fairly low temperature, low enough to be directed upon the hand for a moment, or upon silk or other cloth, or even matches. Perhaps the tiny particles are really solid when they strike the part under treatment, but are liquefied by the heat of the collision. Whatever the action may be, however, the fact remains that a dense, strongly coherent coating is produced, which is said to be amorphous and vitreous, rather than crystalline.

Any desired weight or thickness of deposit may be obtained at will and almost any metal or alloy can be used, so the process would seem to have a wide field of usefulness before it, both from protective and decorative standpoints. While it is yet comparatively new and has not come into extended use, there does not seem to be any good reason why it could not be employed to coat bridges or other forms of structure work, either wholly or at any desired point, as the necessary apparatus is not very cumbersome or

expensive. It is claimed that lead can be sprayed for less than two cents per square foot and one pound can be deposited in less than one minute.

Various other alloys and processes are being proposed from time to time and doubtless some of them will prove to be of real value, but so far as the writer is aware none of them has displaced to any great extent the older protective methods.

The protection of iron and steel by paints and similar materials will be considered in succeeding chapters.

Chapter IV

PAINT MATERIALS

IN the preceding chapter the most important protective coatings for iron and steel (other than those produced by paint and similar substances) were considered, and now we come to the study of these latter materials.

Galvanizing, plating, and the other methods which have been discussed are very widely used and are of the greatest value, but the use of paint is hardly secondary to these and is worthy of the deepest attention. Perhaps one reason why this is true is that the plating methods previously referred to are not always applicable, for some cause or other. For example, it would be impracticable, both from cost and manufacturing standpoints, to galvanize or copper-plate the mighty members of a railroad bridge or similar structure. Also, in much of the piping, railing, machinery, and other iron work of everyday life, it would be altogether too ex-

pensive to apply a plated finish, and even if this was done it would be necessary to use a finishing coat of some other material, if only for the sake of appearance. In other words, the methods previously described are limited in their applicability by their cost and the size of the parts which can be treated. In all such cases, therefore, recourse must be had to some form of paint.

Everyone knows, in a general way, that paint is composed of certain pigments suspended in linseed oil, with perhaps the addition of a drier and some turpentine or benzine, and that it is put on with a brush. In order to study paint intelligently, however, it will be necessary to review some of the facts regarding its manufacture and the ingredients composing it.

In general, there are two ways of making paint. In the first, the pigment is ground in a mill with only enough linseed oil to form a stiff paste, which is thinned when needed for use by mixing with more oil, turpentine, and drier. A little varnish may also be added to improve the quality of the film. In the other method, the pigment is thoroughly mixed with the amount of oil necessary to make a paint of the desired consistency, and

this mixture is then ground by running it through a paint mill several times.

Both of these procedures have certain advantages, but it is doubtful if the pigment and oil can ever be as thoroughly incorporated, when the first method is used, as when they are ground together; so when the best results are expected it is better to obtain the paint ready mixed from the factory. Another point in favor of this is that such a paint is far more likely to have all the ingredients mixed in the right proportions.

For everyone who uses paint, and especially for engineers who may be called upon to draw up specifications or make recommendations regarding it, some knowledge of the materials employed in paint making and the processes by which they are produced is necessary, and the principal ingredients found in the ordinary paints used on metal work will be briefly considered.

The one substance which is common to all paints is linseed oil. This is obtained either by grinding and pressing the seeds of the flax plant or by extracting them with naphtha. The pressed oil contains a good deal of foreign matter, "foots," which may be partly removed by filtration, the rest settling out on

long standing. If the oil is painted upon a strip of glass or other surface and exposed to the air, it will slowly absorb oxygen and become converted into a tough film. With raw oil this forms too slowly, however, for practical purposes, so recourse is had to the process known as boiling, whereby the drying properties of the oil are greatly increased. Heating it to a temperature of 400 degrees F. to 500 degrees F. has the effect of making it considerably darker and more easily dried. The addition of salts of lead or manganese to oil heated to a high temperature also produces this effect, and this was the old method of boiling oil. A very dark oil, however, is objectionable for many purposes and it is now the practice, at least at many places, to make a drier of the metallic oxides by heating them at high temperatures with a small quantity of the oil, and then adding the residue, dissolved in benzine or turpentine, to the main body of oil kept somewhat above the boiling point of water. By this method fuel, time, and oil are saved and the resulting product is lighter in color than with the other processes.

Regarding the quality of the oil thus produced there seems to be a considerable differ-

ence of opinion. Some people assert it is as good in every way as that which has been heated to a high degree with the salts or oxides; others maintain that an inferior grade of oil is produced. Amid these conflicting views it is hard to decide, but it is probable that when it is made into a properly designed paint it will give satisfactory service, at least in many cases.

In making up a paint a certain percentage of raw oil is generally added to the boiled oil, or raw oil may be used alone, a small quantity of a japan or oil drier being added in each case. Japan driers are made by melting resins with salts and oxides of lead and manganese or other metals, afterward thinning the mass with turpentine or light mineral oils. The action of such a drier is very rapid. Oil driers are made, as noted before, by heating linseed oil with metallic salts or oxides to a high temperature and thinning with more oil and volatile solvent.

The oxides of lead and manganese are most widely used in the making of driers. Manganese salts start the drying action and cause the surface to dry quickly. Lead, on the other hand, causes the oxidation to proceed through the film and is generally used in the

larger proportion. Red lead makes paint films brittle; litharge tends to make them very elastic.

A raw linseed-oil paint dries so slowly that it is impractical and not suited for ordinary use, although it would produce an excellent film in time. The addition of a certain amount of drier is justifiable and necessary, therefore, but it must be borne in mind that at least some action continues long after the oil is dry and eventually tends to bring about the destruction of the film. The kind and amount of drier used, accordingly, has a great influence on the life and durability of the paint and close attention should be paid to this point. It is poor economy to sacrifice a year or two of the usefulness of the paint film in order to make it dry a few hours sooner. On the whole, the oil driers do the least harm, but even they should be used in moderation.

Since the tests for the purity of linseed oil are to be found in many text and reference books they will not be given here. According to price conditions and so on, mineral oils, turpentine, rosin and rosin oil, and corn, fish and cottonseed oils may be used to adulterate it. The detection and estima-

tion of these is the work of the analytical chemist and further consideration of them would be out of place here.

Among the other oils which may be added to, or used as substitutes for, linseed, perhaps tung or China wood oil is the most important. When properly boiled and treated it yields a film which is hard and elastic, with heavy body and high gloss. One great advantage of this oil is that it forms paints which will dry in damp atmospheres. It has long been used by the Chinese and Japanese and is finding wide use for marine and waterproof paints, and there is no apparent reason why it should not be used more extensively for protective paints for iron and steel.

Soya bean oil is obtained from the soya bean which grows in Manchuria, although it will also grow well in many parts of the United States. It is very similar to linseed oil, so much so that it is difficult to detect its presence in the latter. Efforts are being made, and with success, to utilize it in the manufacture of paint.

Menhaden or fish oil will be mentioned, as it is used in special paints which are required to stand heat and light, as on smoke-stacks. Such a paint is considerably more expensive

than a linseed-oil paint, so it can be seen that menhaden oil is a valuable aid and not an adulterant, as often claimed. Proper treatment of the oil is very expensive, as the loss by evaporation is large and certain volatile products are formed which are very offensive to the workmen. Mixed with linseed oil, it is used to some extent for making water-proof paints for various purposes and seems to give good satisfaction.

Coming to the materials used for thinning and diluting paints, turpentine is the most valuable. It is the product of the sap of several species of pine trees growing in the South. The sap is collected and distilled with steam, the turpentine passing over and the rosin being left behind. Foreign turpentines differ somewhat in specific gravity and odor, but have the same composition.

When added to paint, turpentine causes the latter to work more easily and increases the spreading power. It evaporates slowly and completely without leaving a stain, and causes more rapid oxidation of the paint oils. The one objection to turpentine is its comparatively high price, and many substitutes are on the market, as such or as adulterants. Some of the best of these are light mineral

oils derived from the refining of petroleum and other substances. In their flash and boiling points they resemble turpentine, possess the same flowing qualities, and apparently are just as good. At any rate they are cheaper and are being used widely. One of these, benzol, may be especially mentioned as it is used very largely in coal-tar and asphaltum paints and in paint and varnish removers.

Experience has shown that the value and durability of any paint depends in large measure on the pigments used, and this is especially true of protective paints for iron and steel. It has been known for many years that certain pigments give better results than others, but it is only recently that efforts have been made to determine the action of some of these materials. Considerable work has been done on this subject and it has been possible to classify pigments as stimulators, inhibitors, and inerts or indeterminates, on the basis of extended researches carried out by several investigators. Finally the American Society for Testing Materials decided to undertake a similar series of tests and the results were so interesting and instructive that they are given on pages 84 to 86. Briefly, the method of conducting the test was to

place pieces of carefully weighed steel in a series of bottles, each of which contained a pigment suspended in distilled water through which air was bubbled. After about three weeks the steel pieces were cleaned, dried, and weighed, the loss in weight being carefully noted. In performing this experiment several investigators worked independently and these results are taken from the Proceedings of The American Society for Testing Materials, Vol. 10, 1910.

In considering these results it must be borne in mind that they are merely indicative of the general nature of the pigments when suspended in water, and it does not necessarily follow that oil paints made from these would show up in service in exact agreement with the recorded test. A pigment suspended in a paint film is under vastly different conditions from one in water, but the results of practical tests are in broad accord with the tabulated data, and it appears that those pigments which, in water suspension, depend upon the inhibitive action of chromate salts or the presence of hydroxylions, through hydrolysis, will, in general, give a good account of themselves when made into an oil paint.

CHART OF FINDINGS OF MEMBERS OF COMMITTEES "D-1" AND "A-5," AMERICAN SOCIETY FOR TESTING MATERIALS

Loss of steel, in grams, in tests carried out on pigments to ascertain their value as rust inhibitors

	Pigment	Gardner No. 1 20 days	Cushman No. 1 & 2 10 days	Walker P. H. No. 2 7.5 days	Cushman No. 2 10 days	Walker W. H. No. 1	Average
1	Zinc Chromate	.0050	.0300	.0094	.0130	.0396	.0194
2	Zinc and Barium Chromate	.0153	.0468	.0034	.0140	.0351	.0229
3	Zinc and Lead Chromate	.0094	.0277	.0153	.0085	.0620	.0246
4	Zinc Oxide	.1524	.0296	.1002	.0085	.0504	.0682
5	Zinc Lead White	.0842	.1712	.0515	.0856	.0456	.0876
6	Barium Chromate	.2333	.0101	.0429	.0094	.1932	.0978
7	Ultramarine Blue	.0247	.3185	.0137	.1865	.0496	.1186
8	Chrome Green (blue tone)	.0860	.2269	.0548	.1240	.2346	.1453
9	Prussian Blue (inhibitive)	.1438	.2267	.0448	.1130	.2671	.1591
10	Lithopone	.0160	.3791	.1274	.1792	....	.1754
11	Willow Charcoal	.1694	.2795	.1439	.1362	.2110	.1880
12	Litharge	.4325	.1932	.0309	.1584	....	.2038
13	Dutch Process White Lead	.2040	.2895	.1781	.1150	.2743	.2122
14	Quick Process White Lead	.2120	.3352	.1288	.1848	.2274	.2176
15	Calcium Sulphate	.3966	.2143	.1759	.1597	.2174	.2328
16	Prince's Metallic Brown	.3774	.2620	.1983	.1408	.1974	.2352
17	Orange Mineral French	.3950	.2724	.1495	.1467	.2526	.2432
18	Calcium Carbonate (Whiting)	.3828	.3620	.1384	.2380	.1208	.2484
19	Sublimed Blue Lead	.3177	.3425	.1001	.2365	....	.2492
20	Lemon Chrome Yellow	.2767	.4067	.1365	.1972	....	.2543
21	Orange Chrome Yellow	.2826	.4203	.1700	.1907	.2150	.2557

22	Medium Chrome Yellow	.2645	.2288	.1763	.1319	.3767	.4090
23	Chrome Green	.2651	.3521	.1453	.1348	.3670	.3265
24	Venetian Red	.2666	.1564	.2375	.1955	.4756	.2682
25	Bone Black	.2674	.4401	.1413	.0921	.3245	.3392
26	Asbestine	.2762	.3405	.2240	.1748	.4025	.2394
27	Keystone Filler	.2881	.1481	.3349	.1366	.4651	.3560
28	Orange Mineral (American)	.2970	.2315	.2065	.1719	.4336	.4416
29	Umber	.3009	.2403	.3817	.1498	.5961	.1365
30	China Clay	.3034	.3212	.2445	.1248	.4770	.3493
31	Calcium Carbonate (precipitated)	.3111	.2616	.2625	.1828	.4910	.3574
32	Red Lead	.3117	.5707	.1717	.1495	.3555	.3112
33	Prussian Blue (neutral)	.3171	.4173	.2415	.1218	.4463	.3584
34	Indian Red	.3228	.4334	.1905	.2617	.3739	.3546
35	American Vermilion	.3270	.3387	.1877	.2612	.4147	.4328
36	Sublimed White Lead	.3300	.3116	.2372	.0982	.5856	.4176
37	Sienna	.3761	.4462	.3085	.2949	.5432	.2876
38	Naples Yellow	.3797	.3846	.2347	.1512	.4800	.6482
39	Prussian Blue (stimulative)	.3825	.5202	.2195	.2055	.4559	.5113
40	Mineral Black	.3993	.3353	.3529	.2017	.8018	.3050
41	Barytes	.4472	.5636	.3841	.2547	.5883	.4454
42	Natural Graphite	.4545	.7165	.3173	.2606	.5437	.4342
43	Bright Red Oxide	.4566	.4429	.3707	.2920	.7896	.3878
44	Acheson Graphite	.4641	.5095	.2789	.3723	.6337	.5262
45	Ochre	.4716		.4315	.2119	.8408	.4022
46	Carbonith White	.4904	.7152				.2655
47	Carbon Black	.5099	.5716	.3751	.4069	.6955	.5003
48	Precipitated Blanc Fixe	.5467	.5064	.5085	.3132	.8806	.5247
49	Lampblack	.7294	.6257	.7096	.2838	1.3098	.7180

CLASSIFICATION OF PIGMENTS BASED ON RESULTS OF TESTS

Inhibitors	Indeterminates	Stimulators
Zinc Lead Chromate	White Lead (quick process, basic carbonate)	Lampblack
Zinc Oxide	Sublimed White Lead (basic sulphate)	Precipitated Barium Sulphate (blanc fixe)
Zinc Chromate	Sublimed Blue Lead	Ochre
Zinc and Barium Chromate	Lithopone	Bright Red Oxide
Zinc Lead White	Orange Mineral (American)	Carbon Black
Prussian Blue (inhibitive)	Red Lead	Graphite No. 2
Chrome Green (blue tone)	Litharge	Barium Sulphate (barytes)
White Lead (Dutch process)	Venetian Red	Graphite No. 1
Ultramarine Blue	Prince's Metallic Brown	Prussian Blue (stimulative)
Willow Charcoal	Calcium Carbonate (whiting)	
	Calcium Carbonate (precipitated)	
	Calcium Sulphate	
	China Clay	
	Asbestine	
	American Vermilion	
	Medium Chrome Yellow	

Regarding the method of manufacture of some of these materials, zinc chromate is a yellow pigment made from zinc salts and potassium dichromate. It is fairly soluble in water and generally contains other chromates and zinc oxide, with some impurities. It has a specific gravity of 3.5 and grinds to a paste in 25 per cent of oil. Considerable drier is required as it is a slow drying material, but it has proved to be one of the most inhibitive of all pigments in use and is valuable in even small amounts in protective paints. Its rather high price is its only disadvantage.

Zinc and barium chromate is made by precipitating a solution of the chlorides of these metals by sodium chromate. It is less soluble than the zinc salt and is a very good inhibitive.

Zinc oxide is one of the most valuable white pigments and is produced by roasting and subliming certain ores of zinc. It is very opaque, has excellent spreading qualities, and is generally mixed with basic carbonate of lead—white lead—for use in white paints. By thus combining these, certain undesirable qualities of both are overcome. For instance, zinc oxide dries to a hard surface which does

not stand changes of temperature as well as the softer lead pigment. On the other hand it tends to eliminate the tendency toward chalking which the lead possesses. It is widely used as a base for delicate colors and in enamels. As has been shown, it is a fairly good inhibitor.

Zinc-lead white is made from zinc-lead ores containing sulphur. The metals are volatilized and oxidized, forming a white smoke or fume composed of about equal parts of zinc oxide and lead sulphate, which is collected in large bags. When placed on the market it is extremely fine, has a specific gravity of 4.4 and grinds in 12 per cent of oil. It is often mixed with white lead and zinc oxide and inert pigments, is very stable chemically, and generally possesses inhibitive qualities.

Barium chromate is pale yellow in color and is made by treating barium chloride with sodium chromate. Its inhibitive value is not particularly good, probably because of impurities.

Ultramarine blue is made by calcining silica, China clay, soda ash, and sulphur in furnaces and grinding the product. It is of a bright blue color, has a specific gravity of

2.4, and grinds in 30 per cent of oil. It tends to turn darker on iron on account of the formation of sulphide of iron, from the sulphur in it, and is not considered a good inhibitive.

Chrome green (blue tone) is made from lead nitrate, sodium chromate, and sulphuric acid, precipitated on white lead and Chinese blue. It contains a variety of impurities, whereby its protective powers are lowered, is a fairly heavy pigment, and grinds in 25 per cent of oil.

Prussian blue is made by mixing solutions of iron sulphate and potassium ferricyanide and oxidizing the resulting precipitate. It is a pretty blue, has a specific gravity of 1.9, and grinds in 55 per cent of oil. It may or may not be inhibitive in character, depending on its freedom from impurities; therefore it should be tested before use. It exerts a marked preservative action on the oil with which it is combined so that a glossy surface is presented even after long exposure.

Lithopone is produced by mixing solutions of zinc sulphate and barium sulphide The resulting precipitate consists of zinc sulphide and barium sulphate; it is filtered off, heated to a high temperature, and dropped into water, whereby it is thoroughly disinte-

grated. It is washed and filtered again, dried and ground. All of these operations require a good deal of care and attention to produce a satisfactory pigment.

Lithopone is very stable and is probably the whitest pigment known, being very widely used in high-grade enamels. Exposed to light and dampness it darkens, but will often regain its whiteness again. It is, therefore, not suited to outside use, by itself, but needs to have a large amount of some stable pigment combined with it. It has a specific gravity of 4.25 and grinds in 13 per cent of oil. As an inhibitive it stands fairly well, but, as noted, is not adapted to outside use unless mixed with other pigments.

Willow charcoal is made by charring certain kinds of wood, and contains a slight amount of alkali, which is probably the cause of its good inhibitive powers. It is a light pigment and grinds to a paste in 33 per cent of oil.

Litharge, lead monoxide, is formed by heating lead intensely for several hours. It is yellowish red, very heavy, and grinds in 9 per cent of oil. It finds extensive use in the manufacture of boiled oils and is an excellent inhibitor.

Basic carbonate-white lead is made in several ways. The old Dutch process consists in placing lead plates or grids in clay pots with dilute acetic acid, stacking the pots up, and covering with tanbark. Fermentation of the latter causes a rise in temperature and the production of carbon dioxide, which acts on the lead in the pots and gives a basic lead carbonate. At the end of two months the white lead is ground in water and dried, being ground later in oil.

The "quick process" requires but two weeks and is carried out by acting on finely divided lead with dilute acetic acid and carbon dioxide, from burning coke, in revolving cylinders.

In the "mild process" no acid is used, the finely divided lead being agitated in water through which air is blown. Hydrate of lead is formed and later carbonated. A very good product, free from all acid, results.

The result of all of these methods is a very valuable pigment of specific gravity 6.8, grinding in 9 per cent of oil. It is very opaque and has much body, but is rather low in spreading power and is generally mixed with zinc oxide or pigments of similar nature. Sulphurous gases blacken it easily and

it has a great tendency to chalk, due to the fact that it is naturally alkaline and thus acts on the linseed oil in the paint. It is generally inhibitive in its action and is widely used.

Calcium sulphate, gypsum, is found in nature and is widely used in paint manufacture. It is very stable, but is somewhat soluble in water and has a tendency to wash out of paint films. Since it is easily ionized in the presence of water, with the formation of large numbers of hydrogen ions, it should not be used on iron or steel as corrosion is certain to occur.

Prince's metallic brown is one of a number of iron ores which are used in paint manufacture. It is found as a natural hydrated iron oxide, or as a carbonate, and is prepared by roasting at a red heat and grinding. It contains a good deal of silica and alumina and is considered a standard pigment for protective paints.

Orange mineral has the same composition as red lead, but a different tone, and is produced by the oxidation of white lead. Owing to the variety of impurities which it contains its inhibitive power is variable.

Calcium carbonate, whiting, is found extensively as chalk. When properly prepared it

has a specific gravity of 2.8 and grinds in 20 per cent of oil. It spreads well and is used to quite an extent, partly on account of its power of neutralizing any free acid in the linseed oil. The artificial form of this material is lighter and requires more oil for grinding. It generally contains impurities which make its use in protective paints inadvisable.

Sublimed blue lead is made by burning a mixture of galena and soft coal. The fumes are drawn through cooling pipes and into large bags. The pigment has a specific gravity of 6.4 and grinds in 10 per cent of oil. It is bluish black in color and has given very good results when mixed with iron oxide or lampblack.

Lemon chrome yellow is a mixture of sulphate and chromate of lead and is made by precipitating a lead salt by bichromate of sodium and sulphuric acid. Owing to its occluded impurities it is not a good inhibitive.

Orange chrome yellow is essentially a mixture of the neutral chromate and basic chromate of lead, and is made by precipitating a lead salt by chromate of sodium and an alkali. It has a specific gravity of 6.9 and grinds in 20 per cent of oil. It contains a

variety of impurities, but its inhibitive power is good if these are not acid in character.

Medium chrome yellow is the pure neutral chromate of lead and is made from a lead salt and sodium chromate. Its specific gravity is 5.8 and it grinds in 30 per cent of oil. The strength of its color depends on the method of manufacture, and it is used as a tinting material. It is liable to carry down impurities during the precipitation and therefore does not possess very reliable inhibitive powers.

Chrome green, oxide of chromium, is made from chromium salts. It is much used in railroad work as it is very permanent and stable. In addition to other desirable qualities it is inhibitive to a slight extent, but its high cost prohibits its use in many cases.

Venetian red is essentially ferric oxide and calcium sulphate, produced by heating iron sulphate and lime. It is not considered a good material to use on iron work on account of its content of calcium sulphate, which, as noted before, is fairly soluble in water and ionizes easily. Some varieties of this pigment are made by mixing oxides of iron with calcium carbonate and sulphate and, as they are free from acid, are safer for use.

Bone black is made by heating bones to a high temperature for several hours and grinding the residue. It contains a large amount of calcium phosphate and carbon, has a specific gravity of 2.68, and grinds in 50 per cent of oil. It is generally an excellent inhibitor and often replaces carbon black and lampblack in dark inhibitive paints.

Asbestine is a natural silicate of magnesia, occurring also in the form known as talcose. Both varieties are very stable and are used in paints, largely to prevent the settling of other pigments and to strengthen the paint film. They are light pigments, grinding in 32 per cent of oil.

China clay is really aluminum silicate and is found in nature. It is a very permanent, fine, white powder and is much used in paints. It is a light pigment and grinds in 28 per cent of oil.

Red lead is a bright red pigment made either by oxidizing litharge in furnaces or by heating it with sodium nitrate in iron pots. According to conditions of manufacture and other details the color varies somewhat. It is widely used for the protection of iron and is considered to be one of the best pigments known. It is generally mixed with oil, when

required for use, in the proportion of thirty
pounds of pigment to one gallon of oil. It
exerts such a drying action on the oil that no
other drier is necessary. Sulphurous gases
tend to turn it brown and it is often mixed
with certain inert materials. Its inhibitive
power varies with the method of manufacture
and the impurities which it contains.

Indian red is the name applied to certain
hematite ores. They vary in shade and phys-
ical characteristics, but are much used in in-
hibitive and other paints.

American vermilion is essentially a basic
chromate of lead, being formed by boiling
white lead and sodium chromate, with the
addition of small amounts of sulphuric acid.
It has a specific gravity of 6.8 and grinds
in 16 per cent of oil. Its very good inhibitive
properties are probably due to the presence
of free chromates and would probably be
increased by omitting the acid treatment.

Sublimed white lead is a basic sulphate
white lead made by volatilizing galena, lead
sulphide. The fumes are oxidized in the air
to a basic sulphate of lead and are drawn
through cooling pipes to bags. It is very fine
pigment of specific gravity 6.2 and grinds in
10 per cent of oil. It is extremely stable in

every way and is not blackened by sulphurous gases, as are many pigments.

Mineral black is made by grinding certain forms of slate and is mainly used as an inert filler for paints. What is called Keystone filler is made from a bituminous schist ore and contains a large amount of silica, with alumina and carbon. It is used widely on iron and steel, especially machinery.

Barytes, barium sulphate, is found in large quantities in nature and is used extensively in paints. It is very stable and can be used as a base for the most delicate colors. It is very heavy and grinds in 10 per cent of oil. Blanc fixe is the artificial form and is made by precipitating a barium salt by a soluble sulphate. In some ways it is a more valuable pigment than the natural form. Both varieties may contain acids and should be tested before application to iron surfaces.

Graphite occurs in two forms, the natural and the artificial. The latter is purer than the other, but both have about the same specific gravity and grind in 45 per cent of oil. Both have an excessive spreading rate and are generally mixed with some of the lead or other heavy pigments. On account of

their conducting power they are not considered good inhibitors and should not be used as contact coats, although otherwise they form very valuable paints and are widely used.

Ochre is similar to umber and sienna and is essentially an iron-oxide pigment. These vary in their chemical composition and physical characteristics and are not often used alone in paints for iron.

Carbon black is made by burning natural gas and is very pure carbon. It is very light, grinds in 84 per cent of oil, and has been used in conjunction with white lead in protective paints, but it now appears to be a stimulator and as such is not safe to be used as a contact coat, although it can be employed very well as an excluder, on top of an inhibitive paint.

Lampblack is made by burning oils and is also a very pure form of carbon. It has a specific gravity of 1.82, grinds in 75 per cent of oil, and has unusual tinting power, wherefore it is used in large quantities for this purpose. Other characteristics are its great stability, its very slow rate of drying, and a preserving action on the oil with which it is combined. It resembles the graphites in

its ability to conduct electricity; therefore it should not be used as a contact coat, but possesses perhaps unusual merit when used as a top coating.

PROTECTIVE PAINTS

FROM the facts which have been presented regarding the manufacture of paint materials and the tests to which they have been subjected, it should be possible to predict, in a general way at least, the behavior of a protective paint, provided we know its composition. It must be noted, however, that there are many things to be considered in designing or passing on the probable value of a paint from its formula or analysis, as the question is not altogether whether a good quality of linseed oil and stimulative or inhibitive pigments have been used, although these points are of great importance.

In the first place, it appears that even though the inhibitive powers of the pigment are the main factor in protecting a painted surface from rust, this action is enhanced greatly by the use of pigments which are good insulators, as far as the ability to conduct a current of electricity is concerned, for

the base. Again, a study of paint films has shown that some are much better excluders or water shedders than others. It has been shown that linseed-oil films are markedly porous, with the result that water soon penetrates to the surface below and, if it is of iron, sets up corrosion. Most dried paint films are porous, although this porosity may be lessened or prevented by the use of varnish, thus producing a film which is a good excluder. By the use of finely ground pigments the size and number of pores in a film may be very materially reduced, but even then the film is not necessarily a water shedder. Certain pigments seem to convey a peculiar property to a film in that it becomes wet with difficulty or not at all. Water rapidly evaporates or runs off from it and apparently none is retained upon the surface or in the pores.

Perhaps the action of different pigments in excluding water from paint films may best be shown by citing an experiment performed and described by Cushman and Gardner. A number of pigments were ground in oil and films made therefrom. It was not possible to make all films of exactly the same thickness, but there is no doubt that these results are roughly indicative of the ability

MOISTURE EXPERIMENTS (CUSHMAN AND GARDNER)

Figures given express gain in weight, i. e., water absorbed

	7 days	14 days	21 days	28 days	35 days	49 days
Iron Oxides (with 2 per cent Zinc Chromate and 2 per cent Gum)	0.032	0.048	0.072	0.092	0.110	0.140
White Lead, D. D.	0.040	0.078	0.111	0.162	0.187	0.264
White Lead and Zinc Oxide	0.043	0.081	0.115	0.163	0.192	0.266
China Clay	0.044	0.086	0.122	0.182	0.219	0.317
Whiting	0.044	0.079	0.114	0.167	0.197	0.277
Zinc Oxide, Barytes and Blanc Fixe	0.048	0.092	0.125	0.183	0.190	0.290
Zinc Lead White	0.049	0.095	0.130	0.181	0.211	0.284
Red Lead	0.049	0.092	0.130	0.187	0.215	0.295
Basic Sulphate-White Lead	0.049	0.092	0.128	0.185	0.213	0.292
Zinc Oxide and Whiting	0.060	0.110	0.156	0.221	0.256	0.352
Zinc Chromate	0.064	0.121	0.176	0.270	0.298	0.417
Barytes and Zinc Oxide	0.064	0.118	0.169	0.240	0.278	0.386
Zinc Oxide	0.065	0.122	0.172	0.244	0.285	0.391
Calcium Sulphate	0.066	0.140	0.212	0.313	0.377	0.555
American Vermilion	0.069	0.140	0.202	0.311	0.349	0.501
White Lead, Barytes and Blanc Fixe	0.074	0.137	0.200	0.294	0.344	0.490
Barytes	0.074	0.138	0.202	0.298	0.336	0.466
Willow Charcoal	0.077	0.154	0.236	0.378	0.459	0.694
Lithopone	0.083	0.156	0.228	0.332	0.380	0.550
Carbon Black	0.084	0.168	0.250	0.391	0.448	0.654

MOISTURE EXPERIMENTS (CUSHMAN AND GARDNER)

Figures given express gain in weight, i. e., water absorbed

	7 days	14 days	21 days	28 days	35 days	49 days
Lead and Zinc Chromate	0.086	0.161	0.226	0.319	0.369	0.497
Chinese Blue (Stimulative)	0.092	0.185	0.276	0.405	0.470	0.671
Venetian Red	0.093	0.190	0.279	0.418	0.508	0.770
Natural Graphite	0.104	0.223	0.350	0.539	0.632	0.951
Medium Chrome Yellow	0.106	0.207	0.300	0.429	0.505	0.725
Bright Red Oxide	0.116	0.240	0.365	0.548	0.662	0.976
Barium and Zinc Chromate	0.116	0.211	0.298	0.430	0.481	0.660
Ultramarine	0.119	0.230	0.336	0.484	0.578	0.814
Prussian Blue (Inhibitive)	0.125	0.246	0.361	0.521	0.619	0.733
Raw Linseed Oil	0.143	0.300	0.449	0.679	0.803	1.201
Lampblack	0.199	0.411	0.641	1.033	1.234	1.873
Blanc Fixe	0.210	0.472	0.744	1.144	1.414	1.944

of these materials to act as excluders. The method of making the test was as follows:

A series of small glass bottles with wide mouths, holding about two ounces, were half filled with concentrated sulphuric acid, and paint films were tightly sealed over the mouths of the bottles, using Canada balsam. The bottles were then carefully labeled, numbered, accurately weighed on chemical balances, finally exposed to air saturated with moisture and kept at constant temperature under a large glass receptacle. The bottles were removed from the receptacle every week and weighed. The increase in weight, due to the amount of moisture which had penetrated the films, and which had been taken up by the sulphuric acid, owing to its hygroscopic nature, was thus determined.

It is interesting to note the effect which a varnish gum has in closing the pores of a vehicle, as shown in this test. Thus iron oxide used alone stands about half way down the list, but when it contained 2 per cent of gum in addition to the oil it stood very high. It has been shown that the addition of a high-grade Kauri gum varnish to a paint increases its protective power considerably, this increase, up to a certain point, corresponding to the amount of varnish added.

Putting together all of the above facts and coming to the practical design and testing of protective paints, The American Society for

Testing Materials has for a long time been carrying on very thorough studies along these lines. The results of these tests, which have been made under service conditions as far as possible, are available in the reports of the Society, but for the sake of the readers who do not have access to them or who do not have time to look them up and go through the many papers, they will be given here in part, as the writer feels they will be of more value than any theoretical discussions could be.

One of the first tests was on the Pennsylvania Railroad bridge over the Susquehanna River at Havre de Grace, Maryland. Nineteen different paints were applied to panels placed on the bridge and to the bridge itself, brushing coats of definite weights. Very careful data were kept of all the conditions of the test, analyses were made of the paints, and everything, including the inspections, was carried out with a great deal of thoroughness. The final results are now available, but it is considered inadvisable to consider them further here, and mention is made only because it is thought that some reader of this volume might wish to make a thorough study of such a test.

TABLE OF INFORMATION REGARDING PAINTS

	Name of Pigment	Wt. of pigment per gal of oil, lb.	Sp. Gr. of paint as received	Grams of paint to panel at 900 sq. ft. spreading rate
1	Dutch Process White Lead	20.49	2.45	61.0
2	Quick Process White Lead	20.34	2.47	62.0
3	Zinc Oxide XX	16.68	2.12	59.0
4	Sublimed White Lead	19.17	2.36	59.0
5	Sublimed Blue Lead	19.17	2.42	61.0
6	Lithopone	12.78	1.80	45.3
7	Zinc Lead White	13.26	1.96	49.4
9	Orange Mineral American	26.91	2.97	74.7
10	Red Lead	26.10	2.93	73.6
12	Bright Red Oxide	15.78	2.05	60.0
14	Venetian Red	9.30	1.52	38.0
15	Metallic Brown	9.51	1.50	37.7
16	Natural Graphite	7.80	1.37	34.4
17	Artificial Graphite	6.63	1.22	30.8
19	{ Lampblack	1.82	1.60	40.2
	{ Natural Barytes	8.92		
20	Willow Charcoal	4.47	1.08	27.0
21	{ Gas Carbon Black	1.39	1.67	50.7
	{ Natural Barytes	10.03		
24	French Yellow Ochre	8.82	1.46	37.0
27	Barytes, Natural	13.38	1.83	46.0
28	Barytes, Precipitated	12.69	1.84	46.0
29	Calcium Carbonate, Whiting	8.22	1.37	34.5

30	Calcium Carbonate, Precipitated.............	7.68	1.35	34.0
31	Calcium Sulphate, Gypsum...................	6.99	1.25	31.4
32	China Clay, Kaolin.........................	8.01	1.34	34.0
33	Asbestine, Silicate of Magnesium...........	8.25	1.38	34.7
34	American Vermilion, Chrome Scarlet.........	20.49	...	64.5
36	Medium Chrome Yellow......................	17.64	...	67.1
39	Zinc Chromate.............................	10.71	1.57	39.2
40	Zinc and Barium Chromate..................	10.35	1.58	40.0
41	Chrome Green, Blue Tone....................	13.32	1.94	49.0
44	Prussian Blue, Water Stimulative...........	5.88	...	30.0
45	Prussian Blue, Water Inhibitive............	5.79	...	34.5
48	Ultramarine Blue..........................	7.20	1.29	32.5
49	Zinc and Lead Chromate....................	14.28	1.92	48.3
51	Magnetic Black Oxide......................	15.0	1.92	48.3

COMPOSITE PAINTS (For details see page 108)

111	Brown	Made from pigments that were inhibitive in the water test.	10.82	1.30	32.7
222	Black		10.86	1.30	32.8
333	White		14.52	1.744	43.8
444	Green		12.77	1.53	38.6
555	Black	Made from pigments that were stimulative in the water test.	9.37	1.125	28.0
666	Brown		11.74	1.41	35.5
777	White		14.55	1.75	44.0
888	Green		14.57	1.75	44.0

COMPOSITION OF SPECIAL FORMULAS

Pigment	Formula	Ingredients	Paint Formula
No. 111	60	Burnt Umber................	22.50
	20	Zinc and Barium Chromates...	7.50
	20	Zinc Lead..................	7.50
		Japan......................	3.40
		Raw Oil....................	59.10
No. 333	35	Zinc Oxide.................	20.90
	45	Zinc Lead..................	26.87
	5	Calcium Carbonate..........	2.98
	15	Silex......................	8.95
		Japan......................	1.56
		Raw Oil....................	38.74
No. 555	40	Lampblack..................	8.18
	40	Natural Graphite............	8.18
	20	Barytes....................	4.09
		Japan......................	8.33
		Raw Oil....................	71.22
No. 777	60	Sublimed White Lead.........	44.80
	20	Blanc Fixe.................	7.46
	20	Gypsum....................	7.46
		Japan......................	1.60
		Raw Oil....................	38.68
No. 222	30	Bone Black.................	13.72
	2	Prussian Blue..............	0.92
	10	XX Zinc...................	4.57
	50	Silex......................	22.86
	8	Calcium Carbonate..........	3.66
		Japan......................	8.33
		Raw Oil....................	45.94
No. 444	60	XX Zinc...................	32.47
	15	Zinc Chromate..............	8.30
	3	Prussian Blue I.............	1.44
	2	Calcium Carbonate..........	1.08
	20	Silex......................	10.83
		Japan......................	2.22
		Raw Oil....................	43.66
No. 666	50	Red Oxide, 62a.............	22.94
	5	Carbon Black...............	2.35
	35	Barytes....................	15.30
	10	Med. Chrome Yellow.........	5.88
		Japan......................	3.20
		Raw Oil....................	50.33
No. 888	5	Chinese Blue, S.............	4.32
	35	Lemon Chrome Yel...........	18.94
	20	Sublimed White Lead.........	16.23
	40	Barytes....................	21.35
		Japan......................	2.35
		Raw Oil....................	38.51

Some time after this test was started the Paint Manufacturers Association of the United States offered to erect and put under observation of Committee ''A-5'' of The American Society for Testing Materials a series of steel panels to which had been applied paints made up with a variety of pigments, used alone and in conjunction with others, and work was started in the autumn of 1908. The table on pages 106 to 108 is taken from the report of Committee A-5, Proceedings of The American Society for Testing Materials, Vol. 10, 1910.

All the pigments were ground in mixture of two parts raw and one part boiled linseed oil, the weight of pigment per gallon of oil being indicated in the table. In preparing the paints for test it was so arranged that the same amount by volume of each pigment would be used in the same quantity of oil, making use of the formula, Specific gravity of pigment $\times$ 3 = pounds pigment per gallon of oil. In order to avoid the introduction of unknown factors, japan driers were not used.

Several hundred steel plates 24 by 36 inches were obtained and one-half of them pickled in sulphuric acid, neutralized in alkali

solution, washed, and preserved from rusting until needed. The painting of the plates was done very carefully under cover, a spreading rate of 900 square feet to the gallon being used on the pickled plates; on the unpickled samples no definite spreading rate was used. The coats were allowed sufficient time to dry thoroughly; three coats were given regularly to the pickled plates upon which the original fifty-one pigments were applied, but in the case of the special formulas only two coats were applied to the black plates.

In a few cases the viscosity of the paste was so great that it was necessary to add a small amount of pure turpentine, but in these the amount of paint applied was increased proportionately so that the weight originally intended was left when the solvent evaporated. In all other cases the paints were used just as they were made.

The painted panels were placed on three fences near Atlantic City, N. J., each of which is 125 feet long and 5 feet high. These were strongly built of yellow pine and carefully designed to serve the purpose for which they were intended.

Several inspections of the panels have been made, the last available results being ob-

tained in April, 1913. The average of the ratings given to each sample by the different inspectors on the second, third, and fourth annual examinations is given on pages 112 to 114.

The ratings assigned to each panel were based on the amount of rust apparent on the painted surface, as well as the degree of checking, chalking, scaling, peeling, cracking, loss of color, and other signs of paint failure shown. The numeral 10 represents the best condition and the paints are given various markings down to zero, which represents failure.

This table is condensed from tables given in the Proceedings of The American Society for Testing Materials.

Shortly after the last inspection it became necessary to remove the test fences, in order to clear the land for building purposes, and those samples which had failed were dropped from further consideration. They included the following: Nos. 1, 2, 3, 6, 7, 27, 28, 29, 30, 31, 32, 33, 45, 48, 222, 333, 777, 2000, 3000, 4000, 90, 100, 5555.

These results are largely self-explanatory and a detailed discussion of them would hardly be possible or necessary at this time,

RESULTS OF INSPECTIONS OF TEST PANELS, ATLANTIC CITY, N. J., BY SUB-COMMITTEE D OF COMMITTEE D-1

	Pigment	Original class in water test	Average Rating 1911 inspection	Average Rating 1912 inspection	Average Rating 1913 inspection
1	Dutch Process White Lead	Inhibitive	3.7	1.9	1.3
2	Quick Process White Lead	Indeterminate	4.2	2.1	1.3
3	Zinc Oxide	Inhibitive	1.5	0.7	0.8
4	Sublimed White Lead	Indeterminate	9.0	8.1	5.9
5	Sublimed Blue Lead	Indeterminate	8.8	9.0	7.2
6	Lithopone	Indeterminate	2.2	0.8	0.4
7	Zinc Lead White	Inhibitive	4.7	4.5	3.3
9	American Orange Mineral	Indeterminate	8.3	6.9	4.0
10	Red Lead	Indeterminate	8.3	8.1	6.3
12	Bright Red Oxide	Stimulative	8.1	6.7	4.5
14	Venetian Red	Inhibitive	8.0	6.4	5.1
15	Prince's Metallic Brown	Inhibitive	6.3	6.2	6.1
16	Natural Graphite	Stimulative	6.8	6.6	6.2
17	Artificial Graphite	Stimulative	5.9	4.4	2.6
19	Lampblack (Barytes)	Stimulative	6.3	5.5	4.2
20	Willow Charcoal	Inhibitive	8.8	8.6	7.9
21	Gas Carbon Black (Nat. Barytes)	Stimulative	7.2	7.0	6.8
24	French Yellow Ochre	Stimulative	5.5	5.8	5.2
27	Natural Barytes	Stimulative	0.7	0.3	0.1
28	Precipitated Barytes (Blanc Fixe)	Indeterminate	1.8	0.7	0.2
29	Calcium Carbonate (Whiting)	Indeterminate	0.0	0.0	0.0
30	Calcium Carbonate (Precipitated)	Indeterminate	0.0	0.0	0.0
31	Calcium Sulphate (Gypsum)	Indeterminate	1.7	0.9	0.2

RESULTS OF INSPECTIONS OF TEST PANELS, ATLANTIC CITY, N. J., BY SUB-COMMITTEE D OF COMMITTEE D-1
—Continued

Pigment	Original class in water test	Average Rating 1911 inspection	Average Rating 1912 inspection	Average Rating 1913 inspection
32 China Clay (Kaolin)	Indeterminate	6.3	2.7	1.3
33 Asbestine (Magnesium Silicate)	Indeterminate	5.1	1.9	1.2
34 American Vermilion (Chrome Scarlet)	Indeterminate	10.0	9.9	9.8
36 Medium Chrome Yellow	Indeterminate	7.7	6.0	5.2
39 Zinc Chromate	Inhibitive	9.5	8.8	8.0
40 Zinc and Barium Chromate	Inhibitive	9.5	8.5	7.8
41 Chrome Green (Blue Tone)	Inhibitive	9.8	8.6	7.6
44 Prussian Blue	Stimulative	9.0	7.8	6.7
45 Prussian Blue	Inhibitive	8.5	7.2	5.0
48 Ultramarine Blue	Inhibitive	0.0	0.0	0.0
49 Zinc and Lead Chromate	Inhibitive	9.7	9.2	8.3
51 Magnetic Black Oxide	.....	9.5	8.6	7.8

COMPOSITE PAINTS

Panel		Average Rating 1911 inspection	Average Rating 1912 inspection	Average Rating 1913 inspection
111 Brown	Made from pigments that were inhibitive in the water test.	8.5	7.8	6.2
222 Black		8.8	5.8	2.8
333 White		4.5	2.7	1.5
444 Green		6.7	5.2	4.2
555 Black	Made from pigments that were stimulative in the water test.	8.2	7.2	5.9
666 Brown		7.7	6.6	6.8
777 White		7.2	5.0	3.0
888 Green		8.0	7.8	7.2

RESULTS OF INSPECTIONS OF TEST PANELS, ATLANTIC CITY, N. J., BY SUB-COMMITTEE D OF COMMITTEE D-1
—*Continued*

Panel	COMPOSITE PAINTS	Original class in water test	Average Rating 1911 inspection	Average Rating 1912 inspection	Average Rating 1913 inspection
2000	1 coat Zinc Chromate, 1 coat Iron Oxide excluder	....	8.1	5.3	3.8
3000	1 coat Lead Chromate, 1 coat Iron Oxide excluder	....	7.3	4.7	3.4
4000	1 coat Red Lead, 1 coat Iron Oxide excluder	....	7.7	5.2	3.4
100	Straight Carbon Black Paint with Turps and Drier	....	6.5	6.3	4.8
90	Straight Lampblack Paint with Turps and Drier	....	5.7	4.2	1.5
5555	Coal Tar Paint over Red Lead	....	5.2	3.7	2.3

but a few comments may not be out of place. First, it will be noticed that not all of the pigments have shown up as might have been expected from the results of the water suspension test, quoted in the preceding chapter. In other words, some of the materials which were considered to be inhibitive in their action showed up considerably inferior to some which were thought to be stimulators. There are probably several reasons why such a result was obtained. It has been previously noted that a pigment in water suspension is under vastly different conditions from one in a paint film, that is, in oil. It will be recalled that in the preparation of the paints the same amount by volume of each pigment was ground in the unit quantity of oil. Pigments vary greatly in the amount of oil which is required to grind them into paste or paint form, and there can be little doubt that different results would be obtained if various quantities of oil had been mixed with each pigment.

Again, the fineness of the pigment makes a great deal of difference to the paint, as it determines the extent to which the pores and voids in the oil film will be filled up, thus producing a more impervious film. Then, too,

the freedom of the pigment from impurities can easily be seen to be of prime importance. In this test the materials were of commercial purity.

In the case of paints made from a combination of pigments, the deviation of the results obtained from those which might have been expected was considerable. In such a case we have to regard the action of several pigments in a film, instead of one, and at present such action is not always easily foretold. There is no doubt that the proper combination of two or more pigments makes a better and more durable paint than one used alone. In the main this effect is mechanical or physical, each component contributing certain properties toward the production of a film having the desired qualities.

On the whole, it seems that these tests show what each of the pigments tested has done, and probably would do regularly, when made up in a certain vehicle and in a certain way, and that valuable data have been obtained for use both in the practical designing of protective paints and in the carrying out of future experimental work.

In working up a paint formula attention must be paid to the particular requirements

of each case, since no one combination will give good results in all situations. For instance, a paint which must stand exposure to light and heat is of different composition from one which would be used in a cool, damp place. It is not possible to consider this question further, but it is hoped that the data which have been given will be of at least some assistance along these lines.

The method of protecting iron, particularly building and structural material, employed by the manufacturers of "Asbestos Protected Metal," is worthy of notice. Briefly, the process consists in cleaning and heating the parts, then immersing them in some asphaltic compound, also kept at a high temperature. Upon removal they are passed through rolls, to secure more perfect union of the steel and the coating compound and remove air bubbles, then through another set of rolls between two sheets of asbestos felt, made from a special, long-fibred material.

Of course, the use of asphaltum in one way or another as a protective agent is not new and when properly prepared it may give very good results. Heating the iron before the application of the coating is an excellent plan, as all moisture is thereby removed from the

surface and pores; the advantage in doing this is easily seen. The asbestos acts as a mechanical protection to keep the underlying coating from injury by blows or scratches and shields it from the destructive action of the sun and air. The final stage of the process is a treatment designed to make the asbestos water-proof, so it would appear that parts protected in this manner should last almost indefinitely.

Coming now to protective materials which are slightly different from the foregoing, so-called baking japans are used widely in finishing a large variety of metal work requiring a decorative finish which is cheap and durable. In general, black japans are made by combining linseed oil and asphalt, gilsonite, stearine pitch, coal-tar pitch, and similar substances at high temperatures. The resulting product is thinned with turpentine, benzine, or light mineral oils, and when applied by spraying or dipping and baked at a temperature ranging from 200 degrees F. to 450 degrees F. or so, will give a more or less thick coating which is quite hard, fairly impervious, and of a high lustre. The baking period, which varies from two to six hours or longer, and the temperature of baking, de-

pend on the composition of the japan. Dull and medium gloss japans are made by grinding the bright japan with lampblack or carbon black in a fine mill. The method of application and baking is the same as given.

Colored japans or enamels are essentially pigments ground in a boiled linseed oil which may or may not contain a percentage of varnish gums. They are generally baked at considerably lower temperatures than the black japans.

The film given by these baking japans is much harder than an ordinary paint film and will stand rougher handling and usage, a circumstance which gives them a marked advantage in many cases. While they are hardly intended for outdoor exposure and perhaps are not as durable and resistant under such conditions as the best oil paints, they give, nevertheless, very good protection even under severe service. Two or three coats may be applied in much less time than it takes for one coat of paint to become thoroughly dry, so this is an added advantage of some importance. Altogether, baking japans furnish a means of producing quickly and cheaply a coating which has good protective and decorative qualities.

An interesting application of this sort of process is in the coating of large pipe for water mains and so on. Many years ago Dr. Robert Angus Smith, an English scientist, patented a method of treating such objects by dipping them in a mixture of coal tar, from which most of the volatile constituents had been distilled, and linseed oil, kept at a high temperature. The part was thoroughly cleaned and coated with linseed oil, which was baked on, then it was coated with the coal-tar mixture and the residual heat of the pipe served to bake this on. In passing, it is worthy of comment that not very much improvement has been made in the matter of coating cast-iron pipes since the time of Dr. Smith. The application of a coal-tar coating does not give very good results on sheet-steel riveted pipe, however, and a more or less soft asphaltum is now used. A material known as maltha and obtained from California petroleum as a residue which remains in the retort after the more volatile portions have distilled off, is used to a large extent for this purpose. The dipping material is thinned with high boiling mineral oils and is heated to a high temperature for application, but the pipe is not baked after-

ward, the coating being allowed to cool in the air.

Sabin has improved this process by the use of asphaltum and linseed oil, whereby it is claimed to be possible to obtain a coating of any desired degree of elasticity by adding the requisite amount of the latter and baking properly. The use of volatile solvents is avoided by heating the compound to 300 degrees F. for application and a thin uniform coating results. After dipping the pipe is allowed to drain for a time, until the excess has run off, which ordinarily takes one half-hour or less. It is then put in the oven, which is heated somewhat above 300 degrees F., and allowed to remain two hours or so, or until the volatile substances have been driven off and the oil oxidized. A tough, hard coating is produced and the Sabin process, as it is called, is finding a wide use. It is interesting to note that the steel underfloors of the roadways and sidewalks of the Williamsburg bridge over the East River in New York City were pickled and coated in this manner, with very satisfactory results.

A coating for steel and wrought-iron pipe, thoroughly protected by some sort of heavy fabric, is much superior to one produced by

simple immersion in a bath of the hot bitum-
inous compound, and the ''National Coat-
ing,'' produced by the manufacturers of Na-
tional pipe, may be mentioned as a sample of
this type.

In applying this the pipe is cleaned and
dried, then dipped at a temperature above
the boiling point of water into a hot bath
of a special refined bituminous compound,
after which it is removed and allowed to
drain in a vertical position and cool. The
next operation consists in placing it in a
winding machine where a strip of fabric,
saturated in the hot compound, is wound
spirally over the surface so as to overlap an
inch or so on each turn; if necessary two or
three layers of fabric may be applied. The
final result is a hard, but tough and elastic,
coating of considerable thickness which is
strengthened and protected by the heavy
fabric embedded in it.

Naturally, gas and water pipes are liable to
undergo rather strenuous treatment before
they are finally laid to rest in the ground, and
an ordinary coating may be badly scraped
and damaged, thus greatly reducing its use-
fulness. A coating such as described above,
however, is very resistant to mechanical in-

jury and should remain in good condition almost indefinitely.

There is still another class of protective materials, known as lacquers, which may be considered briefly here, although they afford relatively very slight protection and are not used to any great extent on iron. In general there are three kinds of lacquers—gum or resin, pyroxylin, and those made by combining these two.

The first kind is made by dissolving shellac, kauri, damar, sandarac, and so on, in alcohol, fusel oil, or other solvents. Resin lacquers are applied by brushing, as a rule.

A pyroxylin lacquer is essentially a solution of cellulose nitrate in amyl acetate. The nitrate is generally made by treating cotton with a mixture of nitric and sulphuric acids, whereby a reaction takes place in which the cellulose unites with two or three molecules of a nitrogen compound, depending on the strength of the acid and the temperature and time of treatment. The cotton is then washed and all acid neutralized, and after drying is dissolved in a suitable solvent. Amyl acetate is perhaps the best, but it is very expensive, so is often adulterated with wood alcohol, acetone, benzine, or other substances.

The finest lacquers of this class are made from nitrated tissue paper, since this gives a whiter and better appearing product than cotton. This "water white" lacquer is used almost exclusively on silverware.

The combination lacquers are made by mixing solutions of pyroxylin and resins, thereby producing a material which has a far wider range of usefulness than either of the preceding. By the proper blending and mixing the most desirable qualities of both of the constituents may be brought out—hardness and covering power may be increased without increasing the flow, and so on. Probably the combinations of pyroxylin and shellac are the best and most widely used.

Any of the above lacquers may be colored by grinding pigments in them or by adding suitable dyes. They are mostly used, of course, for decorative work. All of these materials are applied by dipping, brushing, or spraying, depending on the nature of the work and the qualities of the lacquer, and are allowed to dry in the air or subjected to gentle heat to hasten the process and assist in the production of a harder coating. As noted before, lacquers have a rather limited field of usefulness on iron work, but they are

used very extensively on brass and copper articles, fixtures and the like.

In conclusion, there is one important item which has been mentioned only incidentally before, but which is deserving of thorough treatment and consideration, and that is the proper cleaning of the surfaces of iron and steel parts before paint or other protective materials are applied. Paint which is put on a surface covered with grease or dirt does not come into good contact with the metal and consequently does not adhere to it. Sooner or later the dirt will fall or be knocked off and the paint will come with it. Beams and other parts which are coated with heavy oil or which have been allowed to lie on the ground until they are covered with mud and dirt, should be thoroughly cleaned before painting if it is desired that protection of any permanence shall be secured. Mill-scale is another substance which is almost always found on iron work, especially structural material. It is hard and perhaps has some protective power when firmly attached, but all loose scale should be removed as completely as possible by hammer and chisel or sand-blasting, as it tends to crack off slowly, taking the paint with it and exposing the bare

iron. It is a matter of common experience that when rust once gets started it is very difficult to stop it, so progressive rusting may take place under a paint film which is itself intact and in good condition. It is important, therefore, to see that all surfaces are free from active rust, loose mill-scale, dirt, and other foreign substances, and that they are perfectly dry before painting. In addition, warming the parts slightly, whenever this is possible, just before the paint is applied, also tends to promote better adherence and more satisfactory results all around. It must be remembered, too, that these remarks apply not only to the first, but to all subsequent paintings.

Chapter VI

INFLUENCE OF DIFFERENT ELEMENTS ON THE CORROSION OF IRON

IT has probably occurred to everyone who is forced to rely on protective coatings of one sort or another to keep iron and steel from rust and decay, that this method of combating the corrosion problem is of the same order as locking the barn door after the horse is stolen. In other words, since rusting is a consequence of the tendency of iron to go into solution when in contact with water, why not add something to it or treat it in some way so as to eliminate or decrease this tendency? An enormous amount of labor and material, to say nothing of time, is used up every year in coating and protecting iron from adverse conditions, and with the rapid increase in the demand for this metal a correspondingly greater amount of labor, material, and time is required. Obviously, any procedure which would lessen the need for such thorough protection would be a very real saving.

Definite work along this line is of comparatively recent date, and the available information is perhaps not as complete as could be wished; but enough has been done to throw some light on the possibilities of ultimate success and to enable us to use to good advantage some of the facts which have been obtained.

In effect, of course, the problem resolves itself into the study of the influence of the various elements (meaning the different metals and metalloids) on the process of corrosion. Chemically pure iron is little more than a laboratory curiosity; certainly it is not available for commercial use in building bridges and sky-scrapers, and experiments have shown that, on the whole, it is very little or no more resistant to corrosion than well made wrought iron or steel; so the answer to the problem does not lie in this direction, although this should not be taken to mean that any pains are to be spared in making iron and steel of high purity and as free from segregation as possible. Perhaps a better idea of the difficulties presented in accomplishing these ends may be obtained by reviewing briefly the early stages of the manufacture of iron.

This metal is found in nature principally in the form of the oxide, and by far the largest part of the ore is smelted in blast furnaces, which are a sort of immense stove, 75 or 100 feet in height. The ore, mixed with coke (more rarely with charcoal or coke and anthracite coal) and enough flux (generally limestone) to remove some of the impurities in the form of slag or cinder, is charged in at the top. Air heated to a temperature of several hundred degrees Centigrade is forced at a pressure of about 15 pounds per square inch into the furnace near the bottom, through pipes known as tuyères. This blast is further heated by the combustion of the fuel and passes up through the charge, melting and reducing the ore. The metallic iron formed trickles down and collects on the bottom of the hearth, with the cinder floating on top of it; the furnace is tapped at intervals of several hours, and the iron cast into pigs or sent to the steel mill where it is purified as will be described in the next chapter. The cinder is allowed to escape at longer intervals.

The iron produced in this manner is a comparatively impure material, since it contains very considerable amounts of carbon and silicon, especially, and less of manganese, sul-

phur and phosphorus, with varying quantities of several other elements, depending on the character and quality of the ore. Altogether, these impurities will amount to 6 or 7 per cent. Pig iron is melted and cast into various forms, constituting the gray or cast iron of the foundry, but it can not be rolled or otherwise worked without further treatment. Omitting for the present the details of this subsequent treatment, the product is known as wrought iron or steel, which latter is a rather indefinite term. In these, however, the percentage of other elements will generally be well under 1 per cent, except where one or more of them is added purposely, as in making alloys, or for conferring certain desirable characteristics. It is impossible to remove all of the sulphur, phosphorus, and so on, and if the attempt is made to do so, the iron itself undergoes considerable oxidation, the oxide present mingling with the molten metal and introducing a new and perhaps greater danger.

All the ordinary impurities in iron, with the exception of manganese, are electro-negative to it, which means that a current will flow from one to the other in the presence of an electrolyte. Under such circumstances the

solution of the iron will be hastened, as explained in a preceding chapter, and it will corrode much more quickly. It is in a way reasonable, therefore, for the idea to have arisen that the purer steel and iron can be made, the less subject to corrosion will they be, thus rather tacitly blaming the tendency to rust on the inherent impurities of the iron. Without stopping to discuss the soundness of this view, the fact remains that it is not practicable to refine iron beyond a certain point; hence experiments have been tried to ascertain the effect of adding other elements besides those usually found in iron, in the hope that in some way the end desired might be accomplished by this means.

Taking up first the normal constituents of iron and steel, it appears from the data at hand that silicon rather tends to increase corrosion, although this is contrary to what might be expected as it is well known that high silicon irons are markedly resistant to acid attack. It is generally agreed, however, that the resistance to acid is not always a reliable measure of corrodibility, since many discrepancies are observed and perhaps this is one of them. The silicon content of ordinary steel is not very high, so this element,

when present in normal amounts, probably exerts little effect as far as corrosion is concerned, but even if it did have an inhibitive action it could hardly be used in any quantity as it renders steel weak and brittle.

Sulphur is harmful in its effects, materially increasing the tendency to corrode; even fairly small amounts exert an appreciable influence in this direction.

Manganese is popularly supposed to be the cause of much trouble, and the supposedly greater resistance of the older irons over modern steel has been largely ascribed to their low content of this metal. Recent work, however, shows that it does not play as important a part as has been thought. In the tests conducted by Burgess and Aston the results were not altogether consistent, but in general it appeared that atmospheric corrosion increased with higher manganese content, although in all cases this was less than that observed for pure electrolytic iron. On the whole, probably the influence of manganese, unless it is present in amounts greatly in excess of what would ordinarily be the case, may be considered as practically negligible; at any rate its action is not strongly marked one way or the other.

Phosphorus seems to exert a beneficial effect, rather than otherwise, when present in reasonable quantities. Of course, the phosphorus content of a steel affects the physical properties greatly and hence the permissible amount is low; specifications are usually very strict on this point.

Carbon is another element which determines to a large extent the characteristics of iron and steel, and the amount allowable is rather limited; but from some investigations it appears that the corrodibility of annealed steel rises with carbon content up to about .89 per cent., then decreases. In quenched and tempered steels no decrease in corrodibility could be noted up to .96 per cent. carbon. Aside from this the effect of varying amounts of some of the other normal impurities of iron has apparently not been studied in detail, but it is rather doubtful if results of any particular value would be obtained. These metals and metalloids are always present to some extent in iron and steel; to remove them entirely is a very difficult if not impracticable thing commercially, and in any case the weight of evidence goes to show that pure iron corrodes, in the long run, at a rate little or no different from an ordinary, com-

mercial grade of material, assuming that this
is well made and reasonably free from segre-
gation.   The point is, that none of these ele-
ments, with the possible exception of sulphur,
appears to exert any particular influence,
either good or bad, on the process of corro-
sion when they are present in the amounts
permissible from the standpoint of the physi-
cal properties which they confer.   There
seems to be no reason to hope, therefore, that
any benefits will accrue either from removing
them completely or increasing the amount of
any or all of them over that usually met with.

Some time ago Burgess and Aston carried
out experiments on the alloys produced by
adding various quantities of different metals
to electrolytic iron—that is, iron which had
been deposited from a solution of a salt of
this metal by means of the electric current
and therefore was of great purity.   Care was
taken to exclude impurities as far as possible,
in making up the samples, and after the al-
loys had been brought into proper shape for
testing, small pieces were exposed to the
weather for something less than six months,
then cleaned and the loss in weight noted, and
an accelerated acid corrosion test applied.

Before considering the results it may be

noted that these tests were not made on a commercial grade of iron, the electrolytic material being practically free from carbon, silicon, manganese, sulphur and phosphorus and other impurities so that the effect of these was lost, but while this may be objectionable in some ways there is little doubt that the results indicate, in a general way at least, the influence of the metals tested.

In trying out various grades of commercial irons of different degrees of purity, it was found that some corroded more, some less, than the electrolytic, the samples of the latter representing an average product, as far as composition is concerned. In its ability to withstand acid attack or atmospheric corrosion it did not stand out at all prominently, and these results are in general accord with those obtained by other investigators; that is, on very pure iron rust may be somewhat slower in starting than with the ordinary varieties, but the difference in behavior soon becomes negligible and in the course of an exposure test covering several months it appears that there is no decided superiority one way or the other.

A sample of pure iron containing 1.33 per cent of aluminum showed a slightly decreased

tendency to corrode in the air, but was more
easily attacked by acid. Neither it nor an-
other sample containing a much smaller
amount of aluminum gave results of any par-
ticular interest.

Arsenic confers no especial resisting power
against atmospheric corrosion, even when
used in amounts up to 3.56 per cent. It is
well known that this metal is an objection-
able impurity in sulphuric-acid pickling solu-
tions as it slows down the action consider-
ably, and it has been thought that something
of this sort might be exhibited when it is al-
loyed with iron, but apparently the reverse
is true since the rate of solution in acid be-
comes higher with larger amounts of it pres-
ent.

In any case iron-arsenic alloys possess un-
desirable qualities, such as weakness and brit-
tleness, which would render them unsuited
for structural purposes, aside from the fact
that they are rather difficult to make.

In like manner, the alloys with cobalt do
not present any unusual characteristics. The
resistance to acid attack increases with higher
cobalt content, and this is true of the behav-
ior of the specimens exposed to the weather.
As in the case of arsenic, considerable per-

centages of cobalt would be required to pro-
duce an alloy having sufficient resistance to
corrosion to be of much value. The com-
paratively high cost of the metal is one ob-
jection to the use of such alloys and, further,
the addition of such large quantities of it
changes the properties of iron and steel more
or less profoundly and takes us into the realm
of special steels. This is also true of several
other metals besides cobalt.

The addition of nickel gives results some-
what similar to those obtained with cobalt;
perhaps this might be expected in view of the
close chemical relationship between the two
metals. Nickel, however, confers very fair
resistance to both acid and atmospheric at-
tack and this corresponds in a general way
to the amount of this metal present.

As in previous cases, however, a fairly
large amount of nickel is needed (1 per cent
or over) to produce very decided results from
the standpoint of corrosion, and this in-
creases the cost while altering the physical
properties as well; up to about 3.5 per cent
it gives greater strength, raises the elastic
limit and promotes soundness. Iron-nickel
alloys have properties which have been found
of value for certain purposes, but it is rather

doubtful if they come into wide use for general work solely on the score of decreased corrodibility.

Experiments with silver, tin, tungsten and selenium indicate that these elements when alloyed with iron do not alter very much its tendency to corrode. In the case of silver and selenium the alloys contained only small amounts of these metals and it would be unwise to attempt to draw very definite conclusions as to their action. In any event it is not likely that either would be used very widely, on account of the cost.

With both tin and tungsten there is a tendency toward increased resistance to atmospheric corrosion as the content of these metals in their respective alloys becomes greater, but it is nothing remarkable at any time; the alloys with low tin content display very good resistance to acid attack, but this decreases appreciably with the higher alloys. The corresponding figures for tungsten show up well, but they are irregular and lack consistency. As in the other instances, these metals, to be of much effect, would have to be added in amounts which are sufficient to change the properties of the iron markedly; in general the iron-tin alloys are brittle and lack

strength, while those with tungsten are noted for their great hardness and are used under the name of high-speed tool steels. Obviously they would be unfit for ordinary purposes, aside from cost considerations.

Copper may be regarded as a normal constituent of iron and steel, although it is sometimes present only in the barest traces, but the effects which even small additions of it produce are remarkable and a considerable amount of very careful work has been done in investigating the possibilities which it presents along the line of reducing the tendency of iron to corrode at the least opportunity. The results are so interesting that they are worth considering in some detail.

As long ago as 1901 two experimenters, Stead and Wigham, made some tests on copper- and non-copper-bearing steels and came to the conclusion that, under the conditions of their tests, at least, the steels with copper showed up to better advantage. Within the last few years, however, other experimenters have taken up this subject, and of these Buck has probably done more than anyone else and his work merits more than passing attention.

In a paper read before the annual meeting

of the American Chemical Society at Milwaukee, March 25, 1913, he gave the following information regarding the preparation of the samples and the method of conducting the tests.

In order to avoid the possible uncertainty in comparing different heats of steel with and without copper, and in order that the conditions, except the copper content, should be identical, it was decided for these comparisons to copperize portions of heats, leaving other portions of the same heats in their original conditions.

Three heats were used. One was a regular basic open-hearth of the following analysis:

Carbon	Manganese	Sulphur	Phosphorus
.10	.34	.034	.019

A second basic open-hearth heat was re-phosphorized, giving this analysis:

Carbon	Manganese	Sulphur	Phosphorus
.13	.45	.036	.042

The third heat was regular Bessemer steel of the following analysis:

Carbon	Manganese	Sulphur	Phosphorus
.08	.46	.070	.096

In pouring the open-hearth heats several ingots were first poured without the introduction of copper, then to four ingots sufficient copper was added to obtain in two of them about .15 per cent, and the

other two about .25 per cent copper in the finished product. The Bessemer heat was treated in exactly the same way, except that, since the average Bessemer heat is too small to furnish six ingots of the size desired, only two ingots were copperized, aiming at the same contents as in the case of the open-hearth. The copper was added to the moulds a little at a time as they were filling, and that the resultant steel was uniform in its copper content, was demonstrated by many analyses of the bars and of the finished sheets. Indeed, that copper easily diffuses through the bath of molten steel, and does not segregate on cooling, is a well established fact.

Six ingots were then taken from each of the open-hearth heats, two plain, two with .15 per cent copper and two with .25 per cent copper, and three ingots from the Bessemer heat, one plain, and one with each content of copper.

The fifteen ingots thus prepared were carried through the usual mill operations, each bar as cut and each sheet as rolled being chalk-marked so that no confusion could possibly occur, and in the end each lot was again carefully analyzed as a double check on the operations.

One ingot of each grade of open-hearth was rolled into 16-gauge and the other into 27-gauge sheets, 30 by 96 inches; while in the case of the Bessemer steel, one-half of each ingot was rolled into 16- and the other half into 27-gauge. All grades were subjected to exactly the same treatment, being rolled by the same crews, and annealed in the same furnace at the same time, and the finish was such as to conform with that of the competitive sheets used in this test. From 24 to 36 sheets of each of the 9 grades, both gauges, making 18 lots in all, were then sheared to 24 by 96 inches, thus obtaining a strip 6 inches wide

from each sheet. These strips were sheared into 2 by 4 inch test pieces, stenciled with distinguishing marks, and were used for corrosion tests which will be described later. The 24 by 96 inch sheets were corrugated in the usual way, and eight to twelve sheets of each grade shipped to each of three testing stations. One of these is located in the Pennsylvania coke regions, where the air contains notable amounts of sulphurous and sulphuric acids and other fumes from the coke ovens. In this district iron and steel, unless protected, corrode very fast. Another station is located on the sea coast, where the air carries sodium chloride. The third is in a rural community, where the air is quite pure and free from added corrosive agents.

A sloping wooden framework was erected at each place and the sheets fastened thereon, with the precautions to see that the drip from one sheet did not fall on the next one below. They were thus held several feet from the ground, so that there was a free circulation of air on all sides, and exposed to the weather without a protective coating of any sort except the thin film of oxide normally present on the surface of black sheets.

There were likewise exposed at the same time and under the same conditions sheets of both 16- and 27-gauge, purchased on the open market and showing the following average analysis:

Carbon	Manganese	Sulphur	Phosphorus	Copper
.02	.03	.034	.003	.06-.07

All the sheets were placed in position during November, 1911, and were frequently inspected; by means of the small test pieces cut from the large sheets and exposed at the same time, it was possible to determine the loss of weight of each grade.

First, considering briefly the results of the examinations of the large sheets after varying periods of exposure, at the end of seven months in the coke regions the Bessemer steel sample without copper had failed entirely, while those from the same heat but with copper additions were in very good condition. The same thing was true of the basic open-hearth steels, the copper-bearing samples showing up well, while those without it had failed. One from a re-phosphorized heat, but containing no copper, was in somewhat better condition than the corresponding panels from the other heats, although it was showing the effects of corrosion, while the copper-bearing panels were in good shape.

It was noted that the color of the oxide on the non-copper steels was bright red and loosely adherent. The copper steels were

SAMPLES EXPOSED IN COKE REGIONS NOVEMBER 21, 1911, TO AUGUST 14, 1912

Grade	ANALYSIS						Rel. losses, 100 equals greatest corrosion
	Ga.	Carb.	Mang.	Sul.	Phos.	Cop.	
Bessemer	27	.05	.44	.082	.101	.23	39.09
Bessemer	27	.05	.44	.075	.099	.34	39.61
Bessemer	16	.07	.46	.069	.095	.33	41.57
Open Hearth	27	.10	.46	.035	.043	.17	42.09
Open Hearth	27	.07	.47	.038	.043	.25	42.22
Open Hearth	27	.06	.33	.035	.018	.25	43.27
Open Hearth	27	.06	.35	.036	.018	.16	43.92
Bessemer	16	.08	.45	.070	.094	.21	44.05
Open Hearth	16	.14	.46	.038	.043	.27	46.67
Open Hearth	16	.13	.44	.035	.042	.18	46.67
Open Hearth	16	.10	.35	.033	.019	.23	47.32
Open Hearth	16	.10	.34	.035	.020	.16	48.36
Low C and Mang	27	.02	.03	.036	.003	.07	50.19
Low C and Mang	16	.03	.03	.034	.003	.06	53.20
Open Hearth	16	.13	.45	.035	.042	.00	74.64
Open Hearth	27	.09	.47	.037	.043	.00	78.16
Bessemer	16	.08	.46	.070	.098	.00	91.64
Bessemer	27	.05	.45	.076	.100	.00	96.86
Open Hearth	16	.10	.34	.034	.019	.00	98.82
Open Hearth	27	.06	.35	.033	.018	.00	100.00

SAMPLES EXPOSED AT SEASHORE NOVEMBER 28, 1911, TO SEPTEMBER 7, 1912

Grade	ANALYSIS						Rel. losses, 100 equals greatest corrosion
	Ga.	Carb.	Mang.	Sul.	Phos.	Cop.	
Bessemer............	27	.05	.44	.075	.099	.34	51.12
Bessemer............	27	.05	.44	.082	.101	.23	51.12
Open Hearth.........	27	.07	.47	.038	.043	.25	51.96
Open Hearth.........	27	.10	.46	.035	.043	.17	55.03
Open Hearth.........	27	.06	.33	.035	.018	.25	55.59
Bessemer............	16	.08	.45	.070	.094	.21	56.42
Bessemer............	16	.07	.46	.069	.095	.33	56.70
Open Hearth.........	16	.10	.35	.033	.019	.23	57.54
Open Hearth.........	16	.13	.44	.035	.042	.18	58.94
Open Hearth.........	27	.06	.35	.036	.018	.16	58.94
Open Hearth.........	16	.14	.46	.038	.043	.27	60.90
Open Hearth.........	16	.10	.34	.035	.020	.16	64.81
Low C and Mang.....	27	.02	.03	.036	.003	.07	64.81
Low C and Mang.....	16	.03	.03	.034	.003	.06	65.37
Open Hearth.........	27	.09	.47	.037	.043	.00	65.60
Open Hearth.........	16	.13	.45	.035	.042	.00	70.39
Open Hearth.........	27	.06	.35	.033	.018	.00	87.99
Open Hearth.........	16	.10	.34	.034	.019	.00	88.83
Bessemer............	27	.05	.45	.076	.100	.00	98.32
Bessemer............	16	.08	.46	.070	.098	.00	100.00

SAMPLES EXPOSED IN COUNTRY DECEMBER 3, 1911, TO NOVEMBER 16, 1912

Grade	ANALYSIS						Rel. losses, 100 equals greatest corrosion
	Ga.	Carb.	Mang.	Sul.	Phos.	Cop.	
Open Hearth............	27	.06	.35	.036	.018	.16	51.89
Bessemer.............	27	.05	.44	.075	.099	.34	52.69
Open Hearth............	16	.10	.34	.035	.020	.16	52.69
Bessemer.............	27	.05	.44	.082	.101	.23	53.88
Bessemer.............	16	.07	.46	.069	.095	.33	54.67
Open Hearth............	27	.06	.33	.035	.018	.25	55.07
Open Hearth............	27	.10	.46	.035	.043	.17	55.27
Open Hearth............	16	.13	.44	.035	.042	.18	55.27
Open Hearth............	27	.07	.47	.038	.043	.25	55.67
Open Hearth............	16	.10	.35	.033	.019	.23	55.87
Bessemer.............	16	.08	.45	.070	.094	.21	57.26
Low C and Mang......	16	.03	.03	.034	.003	.06	57.46
Open Hearth............	16	.14	.46	.038	.043	.27	58.25
Low C and Mang......	27	.02	.03	.036	.003	.07	64.42
Open Hearth............	16	.13	.45	.035	.042	.00	68.79
Open Hearth............	27	.09	.47	.037	.043	.00	71.77
Open Hearth............	16	.10	.34	.034	.019	.00	76.54
Bessemer.............	16	.08	.46	.070	.098	.00	90.26
Open Hearth............	27	.06	.35	.033	.018	.00	90.66
Bessemer.............	27	.05	.45	.076	.100	.00	100.00

dark brown and the oxide adhered tenaciously.

An inspection several months later disclosed that the steels without copper had failed completely and fallen to the ground, while the copper steels were still in fair shape. The low-carbon and manganese material, American ingot iron, was in rather bad shape and after about eighteen months of exposure had disappeared entirely although all of the copper-bearing sheets were still in place.

While the samples at the sea-shore exhibited relatively less rapid corrosion than those in the coke regions, the same differences in the behavior of the copper and non-copper steels were shown here as in the other case. In something less than two years all the normal steel samples had failed completely, which was also true of the American ingot iron, with the exception of two sheets, while the copper-bearing steel panels were still intact.

At the test station located in the country district, too, the copper steels showed up to approximately the same advantage, over the normal materials, as at the other stations. Space does not, however, permit of a detailed

discussion of the results of the inspections and in any case a clearer idea of the showings of the various materials under test may perhaps be obtained from a consideration of the results obtained on the small test pieces. It may be noted that each result in the preceding table is the average of six pieces; as mentioned previously these were 2 by 4 inches in size.

These results need no comment or explanation, but it is apparent that some progress in the right direction has been made. Whether it will be possible sometime so to alter the characteristics of iron, by the addition of some other metal or combination of metals, that it will not rust at all or only with difficulty, and at the same time not change its mechanical properties objectionably, seems to be doubtful, although further advances along this line will probably be made as time goes on.

Just now, the best available material of this sort is copper-bearing steel, which is finding a wide and rapidly growing use; anyone can make it and the present output is very large.

Chapter VII

THE CORROSION OF WROUGHT IRON AND STEEL PIPE

IT has been shown in the preceding chapter that iron and steel may be made less susceptible to corrosion by the addition of certain elements, but it is a matter of common experience that even without these additions some parts are more resistant to such attack than others, and brief mention has already been made of the fact that the iron manufactured today is not quite the same, in some respects, as that produced formerly. The substitution of modern methods and machine processes for the old, hand way of refining these materials has resulted in a different product, both chemically and physically, and coincident with these changes in method and product there has been a tremendous increase in the use of iron and steel, and perhaps an equally great alteration of the conditions of service; so it is not strange that a good deal of difference of opinion, doubtless honest

enough at bottom, has arisen regarding the relative merits of the old and new varieties, especially their resistance to corrosion. The controversy over wrought-iron and steel pipe, for instance, has been very animated.

Perhaps one reason for this is that nearly everyone uses pipe, or comes in contact with it in some way; then the conditions to which a steam or water pipe are exposed are rather unusual and just the opposite of what generally obtains. On the whole, ordinary iron work is subjected to a large excess of air containing varying amounts of moisture and gases; only at long intervals, as from rain and snow, does the surface become wet. The inside of a pipe line, on the other hand, is in contact with a large excess of water, which may contain much or little oxygen or air. In a line where the water is frequently drained out of the pipes, or where it holds a large amount of air, it will be seen that the conditions for rapid and severe corrosion are present and it is not surprising that a line, or section of it, may go to pieces in a comparatively short time. When such a case happens it is very easy, and perhaps natural, to ascribe it to inferior materials or something of that sort, and unless trouble is taken

to ascertain all the facts in the case very erroneous notions may, and often do, become current. Such a one is the belief held by some that steel pipe is considerably inferior, in point of corrodibility, to that made from wrought iron.

There is perhaps no doubt that the steel produced ten or fifteen years ago was not the equal in all respects of that turned out to-day, but by reason of the improvements which are being introduced from time to time the quality has risen until it may safely be said that there is no ground for comparing it unfavorably with wrought iron, at least without a fair trial.

It may be remarked that this subject is by no means new, and there is available a good deal of literature concerning it, but it is considered to be worth while to review some of this briefly and, without in the least desiring controversy with any whose opinions or interests lead them to disagree with the conclusions stated therein, to present the results of various investigations in the hope that this may help to clear up any false impressions. Much money is lost every year through ignorance and prejudice, and at least some of this occurs in buying ferrous metals,

since certain varieties of these are claimed to
be superior to others and a higher price is
charged for them. If the facts show that this
extra premium is warranted, well and good;
if not, it is a sheer waste of money.

Before considering the data bearing on
this point, however, it may be well to take
up briefly the processes employed in the
manufacture of these two materials so that
a more definite idea of what each is may be
obtained.

The way in which iron ore is reduced in
the blast furnace, with the production of pig
iron containing several per cent of other met-
als and metalloids, has been previously de-
scribed. As noted, this does not permit of
rolling or similar treatment; therefore, it
must be refined before it is suitable for use
other than in making castings. Iron may be
refined in several ways, but for our purpose
only the puddling furnace and Bessemer con-
verter need be considered, as the terms
wrought iron and steel, as used in the manu-
facture of pipe, refer to the product of these.

In puddling, the iron is melted on a bed of
iron ore which gives up part of its oxygen
to oxidize the carbon, silicon and manganese
and, to a less extent, the sulphur and phos-

phorus. The greater the purity of iron, the higher the temperature at which it melts; therefore, the metal in the furnace becomes pasty after a time, as the impurities are burned out, and is worked into a ball and removed.

This is rolled into bars of convenient size which are cut and piled up, then reheated to a welding temperature and rolled again into a bar of the desired dimensions.

Wrought iron produced in this manner is very pure, the greatest and most objectionable part of the impurities being the slag which is scattered all through the metal and gives it the apparently fibrous structure so characteristic of it after rolling. These fine slag lines are easily detected and form a ready means of distinguishing between wrought iron and that produced by other methods; it is only necessary to smooth down a small spot with a file when they will show up, best under a magnifying glass.

It can be seen that the puddling process is rather slow and expensive, since only a limited amount of metal, a few hundred pounds at most, can be treated at a time, while something like an hour and a half is required for a charge and considerable skill and care are

needed in order to obtain a good product. The presence of 2 per cent or so of slag distributed irregularly throughout the mass can hardly tend to increase the homogeneity, and it is generally accepted that lack of this is of more importance, from the standpoint of corrosion, than the presence of a reasonable amount of impurities thoroughly and uniformly mixed in. Further, it is very hard to weld perfectly sheets or bars several inches in width, so laminations are met with and may give serious trouble.

In the Bessemer process the molten iron from the blast furnace is run into huge mixers, then into big converters, shaped something like an egg, wherein cold air is blown through it, entering by means of tubes in the bottom. The oxygen rapidly burns out the impurities, thereby generating a large amount of heat, so no difficulty is experienced in keeping the metal melted. The length of time the air is blown through is determined by the color of the flame issuing from the mouth of the converter. As might be expected, more or less of the iron is oxidized at the same time; but the addition of a small amount of manganese, for example, will take care of these oxides, so the requisite quan-

tity of this, calculated from an analysis of the iron, is added, together with such other elements as may be needed.

It requires only ten or fifteen minutes to convert as many tons of iron into steel, so in point of speed and general economy the Bessemer process is superior to the other; it is especially adapted to making low-carbon steel and, as a matter of fact, gives a product which is more nearly pure, considered on the score of total impurities, than that from the puddling furnace. As a general proposition, the silicon, carbon, sulphur, manganese, and phosphorus may be lower in the wrought iron than in steel, but the former will contain about two per cent of oxides while in steel these will not run over one- or two-tenths of one per cent. From the nature of the process whatever impurities are present are well distributed, and as the metal is rolled directly into skelp, without cutting and re-welding as in the case of wrought iron, the danger from laminations is greatly reduced.

Up to about twenty-eight years ago hand-puddled iron was used entirely for making pipe; for various reasons steel had not been successfully welded, and as the quantities needed were comparatively small there was

no trouble in supplying the demand. With an increasing use of pipe, however, the discovery that steel could be welded when treated properly, and the discovery of cheaper and better processes of making this material, caused it to be employed more and more and two classes of pipe appeared on the market, iron and steel. With many manufacturers in the field different grades of these appeared, and now there are a number of such; in fact, there is as much difference between some of the wrought irons as there is between wrought iron and the steels, and there is a corresponding disparity between the latter. All of this has tended to increase the confusion; and inasmuch as any new material is liable to be looked upon with suspicion, it is perhaps only natural that there should have arisen much lack of agreement regarding the length of life which iron pipe, as contrasted with that made from steel, might be expected to give.

As a consequence a good deal of experimental work has been done and several investigations of the conditions found in actual service carried out to find the answer to some of these questions.

An experiment conducted somewhat over

twelve years ago by the Bureau of Steam Engineering of the Navy Department on lap-welded Bessemer steel, lap-welded iron, seamless cold-drawn steel and seamless hot-drawn steel boiler tubes, may be of interest.

Care was taken to secure good, representative samples of these materials and analysis showed them to be of the following average composition:

	ANALYSIS			
	Cold-drawn seamless	Hot-drawn seamless	Bessemer steel	Iron
Silicon.............	.005	.005	.008	.024
Sulphur.............	.043	.039	.081	.014
Phosphorus..........	.015	.016	.110	.038
Manganese..........	.50	.49	.31	Trace
Carbon.............	.16	.14	.063	Trace
Oxide..............	.23	.30	.28	1.03

Without going too much into detail, the test consisted in weighing the parts, then immersing them in distilled water, through which air was bubbled, for a total of 64 weeks, divided into four periods of sixteen weeks each. At the end of each period the samples were removed, thoroughly cleaned and weighed. The results may be averaged thus:

AVERAGE LOSS IN GRAMS PER SQUARE INCH

	After 16 Wks.	After 32 Wks.	After 48 Wks.	After 64 Wks.	Total Av. Loss	Comparing Iron as 100
Hot-d'n O. H. Steel......	.3034	.5333	.3510	.5070	1.6947	93.7
Bessemer Steel..........	.3147	.4950	.4043	.4945	1.7085	94.5
Cold-d'n O. H. Steel.....	.3232	.5564	.4502	.5017	1.8315	101.3
Charcoal Iron...........	.3326	.5896	.3966	.4893	1.8081	100.

It will be seen by comparing the figures of loss given above that there was no great difference in the behavior of these four classes of materials, as far as loss in weight is concerned; the charcoal-iron samples, which showed the greatest initial loss, ending up with a decrease about 6.3 per cent larger than that of the open-hearth hot-drawn tubes, which suffered the least.

From data collected by the American Society for Testing Materials, 1908, and experiments reported in the *Iron Age,* the table on page 159 has been drawn up summarizing the results of a number of other laboratory tests, largely on wrought iron and steel skelp. The specimens were exposed to the weather or immersed in different kinds of water and the loss in weight determined at the end of the experiment.

These results show that even the steel manufactured fifteen years ago was slightly bet-

INVESTIGATIONS ON THE CORROSION OF WROUGHT IRON AND STEEL

Authority	Date	Conditions of test	Duration of test	Material tested	Rel. loss of weight, per cent
Prof. H. M. Howe........	1897	Sea water, norm. temp.	2 years	Steel skelp / W. I. skelp	117 / 100
Prof. H. M. Howe........	1897	River water, norm. temp.	2 years	Steel skelp, / W. I. skelp	94 / 100
Prof. H. M. Howe........	1897	Weather	2 years	Steel skelp / W. I. skelp	103 / 100
U. S. Navy Department......	1901 / 1901	Aerated, dist. water norm. temp.	64 weeks	Charc'l iron / Pipe steel	100 / 94.5
National Tube Co......	1904	Aerated brine, norm. temp.	6 months	Puddled iron / Pipe steel	100 / 106
National Tube Co......	1905	Aerated water, 180° F.	3 months	Puddled iron / Pipe steel	100 / 90.6
National Tube Co......	1906	Aerated brine, 180° F.	3 months	Charc'l iron / Puddled iron / Pipe steel	80 / 100 / 75.3
Prof. H. M. Howe......	1906	Sea water, 180° F. aerated	3 mos.	Charc'l iron / Puddled iron / Pipe steel	94.4 / 100 / 94.2

ter than the wrought and charcoal irons of the same period.

But while laboratory tests are useful, in giving indications of what may be expected in practice, the results obtained in actual service are naturally more reliable, so about the time the last of the tests were being carried out, a new line of investigation in the shape of trial installations was started.

Prof. Thomson put in a hot-water line, using wrought-iron and steel pipe alternately, so that they would all be subjected to the same conditions. After a year of service he concluded that steel might be expected to stand up about 7.5 per cent longer, under such conditions, than wrought iron.

A short time later a test carried out under similar circumstances under the auspices of the American Society of Heating and Ventilating Engineers, using steel and iron pipes supplied by several makers, checked up closely enough with the previous one and the report of the trial concludes:

We believe (this test) demonstrates that modern steel pipe of good quality is at least as durable as modern strictly wrought-iron pipe of good quality and is very much superior to a poor quality of wrought iron in this class of work.

Various other tests carried out by different observers under a variety of conditions have led to the same general conclusion. Thus, several experiments conducted by the Pittsburg Coal Co. and the H. C. Frick Coke Co., to mention only two, wherein the samples were immersed in running mine water, which generally contains considerable quantities of acid, show that steel corrodes at no greater rate than wrought iron. Again, the work of Howe and Stoughton gave results in broad agreement with this. Commenting on the tests of these two experimenters and the evidence which they have collected, Alfred Sang says in his book:

Of ten different tests made by different observers in different places, seven resulted decisively in favor of steel; in the other three cases the results were very slightly in favor of the iron, but in only one of the latter was the material of modern manufacture.

The tests which resulted in favor of steel were as follows, all except the two first being carried to destruction: Seven months in hot, aerated salt water; sixteen months buried in dampened ashes; exposed to sulphuric acid coal-lime water; in railroad interlocking and signal service; in locomotive boiler service.

It was also found that steel tubes made in 1906 pitted much less than those of 1897 from the same makers, indicating the superiority of modern steel

over that of some years back in this particular respect.

Not all of the work on this subject has been confined, however, to either laboratory or short installation tests, and at least two rather extended investigations have been undertaken on pipe lines as they are found in service. The first was conducted by Prof. Woolson on some of the public bath houses of New York City, where much trouble was being encountered from the rapid corrosion and consequent leaking of the hot-water pipes.

A thorough examination of the situation showed that conditions in these bath houses were not materially different from those found in similar installations in other places. Croton water was used, being heated in various standard types of heaters to a temperature of 160 degrees to 200 degrees F. The quantity of water passing could not be determined, but it was considerable, as many thousands of baths were, and are, given in some of these places during the hot weather. It developed, further, that all the pipe which had been in use four years or over had begun to give trouble, and in a few places pipe only two or three years old had perforated.

In all, eleven houses were inspected, but for

various reasons samples could be collected from only eight; from these eighty-nine specimens, perforated and worthless, were obtained for examination. They varied in size from ¾ inch to 4 inches in diameter, the majority being 1½ to 2 inches.

Small pieces were sawed from each of the specimens, crushed, and the fracture carefully examined by two experts independently to determine whether the material was wrought iron or steel; chemical analyses were then made of all samples which were at all doubtful in classification. The results of these tests were further checked to avoid all possibility of error.

ANALYSES OF PIPE FROM NEW YORK CITY BATH HOUSES

Manganese, Per Cent	Carbon, Per Cent	Oxide, Per Cent	Classified as
.48.....................	.09	.20	Steel
.32.....................	.08	.26	Steel
.42.....................	.08	.21	Steel
.38.....................	.08	.30	Steel
.50.....................	.08	.38	Steel
Trace..................	Trace	2.85	Wrought iron
Trace..................	Trace	2.40	Wrought iron
Trace..................	Trace	2.20	Wrought iron
Trace..................	Trace	2.50	Wrought iron
Trace.	Trace	1.75	Wrought iron

As a matter of interest, in showing the difference between the two kinds of metal, the table on page 163 presents typical results of the chemical analysis.

From all this work it was decided that seventeen out of the eighty-nine samples were wrought iron; these had come from six of the eight houses yielding samples. Of the other two, no samples were examined from one and those collected from the last were proved to be steel. The above data may be arranged in tabular form as follows:

BATH HOUSES AND SAMPLES OBTAINED FROM EACH

Material Supplied	Bath House	Classification
Probably steel..........	11th St.	2 Iron, 6 Steel
Probably steel..........	76th St.	2 Iron, 5 Steel
Not certain.............	23d St.	2 Iron, 4 Steel
Steel...................	41st St.	5 Iron, 7 Steel
Steel...................	Rivington St.	2 Iron, 23 Steel
Steel...................	109th St.	4 Iron, 11 Steel
		17 56

Total of mixed samples................................73
Steel, Allen Street................................16 Steel
Total of all samples................................89

The contract specifications for all except two of these houses called for wrought-iron pipe, galvanized, but plumbers and dealers

often do not make any close distinction be-
tween iron and steel pipe, so the latter may
be supplied alone or mixed with the other. A
few years ago many mills were making both
kinds of pipe and it would be very easy to
mix them in shipment.

However that may be, it will be seen that
of the mixed samples 23 per cent were
wrought-iron and, bearing in mind that the
two kinds of pipe were used indiscriminately,
therefore all exposed to the same conditions,
that all samples were tested to destruction
and that probably not more than 10 per cent
of the welded pipe on the market is wrought
iron, it appears that steel showed up to very
fair advantage.

After his investigation Prof. Woolson de-
cided:

In my judgment, from the evidence collected, there
was absolutely no difference in the corrosion of the
two classes of pipe. They appeared to be equally sus-
ceptible to the attack.

A similar study was made by Dr. Walker
in an attempt to determine how these ma-
terials stood up in service when both were
used in the same system, being separated

from each other only by a coupling. Under these circumstances the wrought-iron and steel pipe would be subjected to as nearly identical conditions as could be obtained, so a fair basis of comparison should be afforded.

Briefly, the method pursued was to examine a large number of steam and hot-water systems operating in different places and under different conditions and to collect samples of wrought iron and steel pipe. It chanced that the majority of the samples collected came from hot and cold-water feed systems, but enough were obtained from live and exhaust-steam lines and other installations to make the results of general interest.

The specimens were split lengthwise and carefully cleaned of rust and accumulated scale by the use of ammonium-citrate solution, which does not attack iron, after which the extent of corrosion was calculated by measuring with a micrometer, the ten deepest pits occurring within a length of about 12 inches.

In all, it was possible to obtain sixty-four comparisons between iron and steel and the results may be summed up as shown in the table at the top of page 167.

COMPARATIVE CORROSION OF WROUGHT-IRON AND STEEL PIPE

Instances where iron corroded more than steel. . 20
Instances where steel corroded more than iron. . 18
Instances where iron and steel corroded equally. 9
Instances where corrosion was negligible. 17

In the light of the facts brought out by this work, Dr. Walker felt justified in concluding that on the average there is no difference in the corrosion of iron and steel pipe.

Immersion in sulphuric acid of a certain strength has been used as a means of determining the comparative resistance to corrosion of different samples of iron and steel, and as an interesting sidelight to the above work, Dr. Walker conducted some experiments to find out whether this test has any real value. As he reports it:

In order to show what relation may exist between the so-called acid corrosion test and the real corrosion as found in service, eleven pairs of iron and steel were selected and subjected to 20 per cent sulphuric acid for four hours at room temperature. Four pairs were selected in which the steel was decidedly better than the iron in service, four in which the iron had shown decidedly better than the steel, and three in which there was no difference between the two metals.

In six instances the relative corrosion as shown by the sulphuric acid test corresponded with the cor-

rosion as found in service. In five instances corrosion as shown by the acid test was exactly contrary to that found in service. Although the greatest care was taken to have the specimen of the same size, cleaned in the same way, and in the same physical condition, the results show that no reliance can be placed in this accelerated acid test, but that it may be entirely erroneous and very misleading. Not only did the acid test not agree with the service test when steel was compared with iron, but the steels failed to agree among themselves, and the irons showed no agreement when considered by themselves.

It may be added that these conclusions have been reached by other investigators, working independently. After all, it appears that, no matter whether one is testing pipe or paint or almost anything else, an actual service test is the only really reliable criterion of merit, or the lack of it.

Viewing impartially all of the data presented so far, there seems to be little to choose between wrought-iron and steel pipe, on the whole, as regards their resistance to corrosive influences, but one point may be mentioned with reference to the manner in which these materials corrode. With steel the rusting takes place more or less uniformly over the surface, while wrought iron shows a decided inclination to form deep pits. That this is a dangerous tendency can hardly be

doubted: to paraphrase an old saying, a pipe wall is no stronger than its thinnest spot; therefore, to the extent in which wrought iron exhibits this defect in greater measure than steel, it may be considered correspondingly inferior to the latter.

In the course of the investigation mentioned above, Dr. Walker found that in the most corroded samples (those being practically worthless) the average depth of pitting was .130 of an inch for the iron and .118 for the steel. Likewise, it was found that of twenty-six samples of iron pipe removed from hot-water boiler-feed lines in the power plants of the H. C. Frick Coke Co. the average of the deepest pit in each was .112 of an inch, while the average of twenty-six steel samples taken from the same lines was .108. Of course, these differences are not at all startling, but they would seem to indicate a weak point in wrought pipe.

THE END

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